VOLUME 6 JUNE, 1932 NUMBER 6

NATIONAL
RESEARCH COUNCIL
of CANADA

CANADIAN JOURNAL OF RESEARCH

CANADA

Published under the authority
of the
Chairman of the Committee of the
Privy Council on Scientific and Industrial Research

OTTAWA • CANADA

CONTENTS

* * *

Publication and Subscriptions

The Canadian Journal of Research is published monthly by the National Research Council of Canada, Ottawa, to which address all correspondence should be directed.

The subscription rate is $3.00 per year to any part of the world. Single copies are thirty-five cents each.

Canadian Journal *of* Research

Issued by THE NATIONAL RESEARCH COUNCIL *of* CANADA

VOLUME 6 JUNE, 1932 NUMBER 6

THE FLOW OF HEAT THROUGH PLATES[1]

BY R. RUEDY[2]

Abstract

The speed is calculated with which the steady flow of heat is established in a slab of uniform temperature after one boundary plane has been suddenly brought to a higher temperature, or when the temperature of both planes is changed. In both cases the flow of heat may be expressed by means of simple theta functions, and the law of approach to the steady state may be used for determining the diffusivity of the material. When one boundary plane undergoes sinusoidal variations in temperature while the other is maintained at a constant level, a finite thickness is found for which, in the steady state, the heat flowing in or out during one half-cycle reaches its highest value.

The Steady State in the Plate Method

When the "plate" method is used for measuring the heat conductivity of solid bodies, one side of a slab is more or less suddenly brought into contact with a source of heat at constant temperature, while the other side is kept cool. Heat begins to flow through the slab, and when a steady state is reached, the coefficient of heat conductivity, k, is determined. Losses which would be caused by radiation, conduction and convection through the rest of the boundary surface are prevented with the aid of a guard ring surrounding the slab. How closely the heat conductivities may be ascertained depends on the accuracy with which the thickness of the plate, the temperatures of the two walls, and the heat energy, Q, furnished to one side or drawn from the colder end, may be measured. The coefficient k is determined from the formula

$$k(c.g.s.) = \frac{Q(\text{watts}) \times b(\text{cm.})}{4.184A(\text{sq. cm.}) \times (v_1 - v_0)\ \text{deg. C.}}$$

where $v_1 - v_0$ is the temperature difference maintained between the two boundary planes. As it is not practicable, in general, to measure the thickness to within less than 0.1 mm. it is desirable to test slabs at least 5, or better, 10 mm. thick in order to keep the possible error below 2%. For a temperature difference of 15° C., an interval over which k may be considered as being constant, an

[1] *Manuscript received May 12, 1932.*

Contribution from the National Research Laboratories, Ottawa, Canada. This paper was read at the meeting of the Royal Society of Canada, May 1932.

[2] *Junior Research Investigator, National Research Council, Ottawa.*

error of 0.2° C. means an uncertainty of 1.3%. The energy, Q, furnished, computed from the current measured to within 0.002 amp. and the voltage read to within 0.04 volt, is known with an accuracy of between ½ and 1%, so that the uncertainties entering into the value of k will not be below ±2% (2). The precision may be improved by using thicker plates, but when many measurements have to be made the question arises as to how much longer it will take for the steady state to be established. While it is also possible to increase the temperature difference between the hot and the cold plane, the changé of k with temperature may introduce new errors.

When at the beginning of the experiment the temperature in a slab of thickness b, specific heat c and density s, is a function, $f(z)$, of the distance z from the cold wall of the slab, and is equal to zero at time t equal to zero, while the ends are kept at the temperatures $F_0(t)$ and $F_b(t)$ during the interval from $t=\lambda$ to $t=t$, then the temperature v at any distance z is at any instant t represented by the following formula (1, p. 69).

$$v=\frac{2}{b}\sum_{n=1}^{\infty}\epsilon^{-n^2\frac{\pi^2}{b^2}\varkappa t}\sin n\frac{\pi}{b}z\left[\int_0^b f(z)\sin n\frac{\pi}{b}z\,dz+n\frac{\pi}{b}\varkappa\int_0^t\epsilon^{+n^2\frac{\pi^2}{b^2}\varkappa\lambda}\left(F_0(\lambda)-(-1)^n F_b(\lambda)\right)d\lambda\right],$$

where $\varkappa=\frac{k}{cs}$ is the diffusivity of the material.

In the simplest case the temperature is constant throughout the thickness, and one side of the slab is maintained at this temperature which may, therefore, be chosen as the zero point so that $f(z)$ becomes equal to zero. The first term in the brackets in the general equation vanishes, so that $F_b(z)=V$ being the constant temperature at the hot side, the relation reduces as follows:

$$v=-2\frac{\pi}{b^2}\varkappa V\sum_{n=1}^{\infty}\epsilon^{-n^2\frac{\pi^2}{b^2}\varkappa}\,n\sin n\frac{\pi}{b}z\int_0^t(-1)^n\epsilon^{+n^2\frac{\pi^2}{b^2}\varkappa\lambda}\,d\lambda.$$

Integrating and taking into account the fact that

$$\sin\frac{\pi}{b}z-\tfrac{1}{2}\sin\frac{2\pi}{b}z+\tfrac{1}{3}\sin\frac{3\pi}{b}z-\ldots\ldots=\frac{\pi}{2b}z,$$

the equation becomes

$$v=V\left(\frac{z}{b}+\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\epsilon^{-n^2\frac{\pi^2}{b^2}\varkappa t}\sin n\frac{\pi}{b}z\right).$$

The heat C flowing through unit area at a distance z and time t is obtained by differentiating v with respect to z and multiplying by k.

$$C=-k\frac{V}{b}\left(1+\sum_{n=1}^{\infty}(-1)^n\epsilon^{-n^2\frac{\pi^2}{b^2}\varkappa t}\cos n\frac{\pi}{b}z\right)$$

or

$$C=-k\frac{V}{b}\theta(z/b,q)$$

where θ is the symbol for the theta function and $q=\epsilon^{-\frac{\pi^2}{b^2}\varkappa t}$. The heat directly measured and flowing into the slab from the hot side $z=b$ is therefore

given by the expression

$$C_b = -k\frac{V}{b}\Theta_3(o, q) = C^0\Theta_3(o, q),$$

whereas the heat penetrating into unit area of the cold wall is

$$C_0 = -k\frac{V}{b}\Theta_0(o, q) = C^0\Theta_0(o, q),$$

where C^0 is the heat flow $\left(-\frac{kV}{b}\right)$ in the steady state. The values of these theta functions are listed in convenient recently issued tables (3). As an illustration of the rate at which the steady state is established Table I shows the times in seconds in which certain fractions θ_3 and θ_0 of the final heat flow are reached in the case of a slab of sulphur 3.14 cm. thick (conductivity k, 0.0005; specific heat, 0.17; density, 2.0; and therefore $\varkappa$, 0.00147), or slightly compressed spruce of 16% moisture content, the flow being measured parallel to the grain (specific heat, 0.33; density, 0.4). Under the conditions stated the coefficient of heat conductivity is the same for sulphur and spruce but on account of the smaller value of cs a higher value for $\varkappa$ (0.0038) results for spruce,

TABLE I

TRANSIENT STATE OF HEAT FLOW

$\varkappa\frac{\pi^2}{b^2}t$	$\exp.\left(-\varkappa\frac{\pi^2}{b^2}t\right)$	θ_3	θ_0	Time in sec. $b=\pi$ cm.		
				Sulphur	Spruce	Air
1.53	0.2176	1.439	0.569	1041	404	8.6
1.95	0.1428	1.286	0.715	1327	515	10.9
2.33	0.0975	1.195	0.805	1585		
2.71	0.066	1.132	0.868	1843		
3.21	0.0400	1.080	0.92	2184		
3.79	0.0250	1.050	0.950	2578	1000	21.2
4.27	0.0140	1.028	0.972	2905	1127	23.9
5.11	0.0060	1.012	0.988	3476	1348	28.5
5.38	0.0046	1.009	0.9908	3660	1420	30.0
6.81	0.0010	1.002	0.998	4633	1797	38.0
7.61	0.0005	1.001	0.999	5177	2008	42.5

and less time is needed for reaching the steady state in which $\theta_3=\theta_0=1$. The times given for sulphur also apply to wood fibre (k, 0.00015; c, 0.31; s, 0.33; $\varkappa$, 0.00146). For any other material they may be found by dividing the figures of the first column by $\varkappa$. As is to be expected, the rate at which heat flows at the beginning from the hot side into the slab is larger than the amount flowing in the steady state because the material must be heated up. Near the cold side, on the contrary, there is practically no heat flowing until $\frac{\pi^2}{b^2}\varkappa t$ or $\varkappa t$, in the present case, exceeds a value of about 0.23; after it has become equal to 0.3, the flow is 0.002 of the final value C_0, at 0.6 equal to 0.074 C^0, at 1.0 equal to 0.3 C^0, etc. Halfway between the two side-walls the number

of calories passing through unit area changes with time according to the expression

$$C_{\frac{1}{2}} = 2C_0 \left(\tfrac{1}{2} - \epsilon^{-4\frac{\pi^2}{b^2}\varkappa t} + \epsilon^{-16\frac{\pi^2}{b^2}\varkappa t} - \epsilon^{-36\frac{\pi^2}{b^2}\varkappa t} + \ldots \right).$$

Here the flow has already reached the fraction 0.63 of its final value at a time when practically no heat has started to flow at the cold end. Each section has its own law governing the velocity with which the steady state is attained, because the parts near the hot plate have to transfer energy to the colder parts, whereas, toward the cold side, where this task is easier, it takes an appreciable time for the heat to arrive. From the moment, therefore, at which in the ideal case one side of the slab is suddenly brought to the desired temperature, until the time when the temperature gradient has become constant throughout the thickness, the shape of the temperature waves penetrating the plate varies from point to point so that no definite velocity of propagation can be assigned to the wave fronts. Moreover, the equation is not meant to apply to minute intervals of time or space, such as the transfer of heat from molecule to molecule, because this exchange is not governed by k, c and s only.

The last column of Table I gives the results for the velocity of heat transmission between an upper hot and a lower cold layer of air (k, 0.000055; c, 0.237; s, 0.00129; $\varkappa$, 0.179). On account of the low density the steady state is rapidly established despite the low heat conductivity k. The figures would not apply if a layer placed between the hot and cold "plates" were considered on account of the finite contact resistance to heat flow between the solid walls and the neighboring air layers. Apart from radiation and convection the quantity of heat flowing in the steady state from 1 sq. cm. of a horizontal plate, kept at temperature v_1, into the air layers below it where the temperature is v_2, is given in cal. per sq. cm. per sec., by the formula

$$C = \alpha_{12}(v_1 - v_2) = 0.000077\sqrt[4]{v_1 - v_2}\,(v_1 - v_2).$$

The fourth root changes only from 1.8 to 3 when the temperature difference $(v_1 - v_2)$ varies from 10.5 to 81° C., the range over which the formula has been verified (4, p. 54). On going from the solid wall into the air layers, the temperature drops fairly rapidly at first and then assumes the value which it has in the layers farther away from the surface. The thickness of these boundary layers is of the order of 0.4 cm. for air at ordinary pressures. For the range of temperature differences tested the heat passing from the plate into the air has nearly the same value as if the temperature differences were established between air layers 0.3 to 0.4 cm. thick, but the gradient is not linear and the change with time will follow a different law. On the other hand, when a slab of material possessing the heat conductivity k_3 is separated from the hot plate by an air space several mm. wide, the coefficient of heat conductivity k of the assembly is given by the expression

$$k = \frac{1}{\frac{1}{\alpha_{12}} + \frac{1}{\alpha_{23}} + \frac{1}{k_3}} \approx \frac{k_3}{\frac{2k_3}{\alpha_{12}} + 1}.$$

The higher the value of k_3 the larger will be the change in k_3 but this change is negligible for very good insulators.

As it will take nine times longer, when one plate is three times as thick as the other, to get the same fraction C_b/C^0 of the steady current C^0, 15 to 30 min. should be ample for thicknesses below 1 cm. to arrive at the steady state. If C_b is measured at a few intervals with V maintained constant automatically, the value of k can be checked and the diffusivity determined at the same time.

Slight Annealing or Quenching of a Slab

The same functions appear when the case is treated in which a thin slab at uniform temperature is suddenly plunged into a bath maintained at $V°$ C. The first term in the brackets of the general formula is then the one that remains

$$v=\frac{2}{b}\sum_{n=1}^{\infty}\epsilon^{-n^2\frac{\pi^2}{b^2}\varkappa t}\sin n\frac{\pi}{b}z\int_0^b f(z)\sin n\frac{\pi}{b}z\,dz,$$

or

$$v=\frac{4V}{b}\left(\epsilon^{-\frac{\pi^2}{b^2}\varkappa t}\sin\pi\frac{z}{b}+\tfrac{1}{3}\epsilon^{-9\frac{\pi^2}{b^2}\varkappa t}\sin 3\pi\frac{z}{b}+\ldots\right),$$

and

$$C=-k\frac{dv}{dz}=\pm 4V\frac{k}{b}\left(\epsilon^{-\frac{\pi^2}{b^2}\varkappa t}\cos\pi\frac{z}{b}+\epsilon^{-9\frac{\pi^2}{b^2}\varkappa t}\cos 3\pi\frac{z}{b}+\ldots\right),$$

a formula which has the same value at z and $(b-z)$. At any distance z and time t the flow of heat through unit area from the two boundary planes into the slab is the resultant of a number of sinusoidal heat waves $4k\frac{V}{b}\cos\pi\frac{z}{b}$; $4k\frac{V}{b}\cos 3\pi\frac{z}{b}$ etc. The higher their order n the more rapidly do these waves diminish, so that after a certain interval, t, only the longest wave is responsible for the heat transfer. The series occurring in the formula is once more a theta function:

$$C=4k\frac{V}{b}\theta_2\left(z/b,q\right),\text{ with }\epsilon^{-\frac{\pi^2}{b^2}\varkappa t}=q^{1/4}.$$

One Boundary Plane at a Fluctuating Temperature

When, in the "plate" method of measuring heat conductivity, one side of the slab is brought into close contact with a surface heated by alternating current, a steady state will be reached, in the course of time, such that the heat flowing into the plate through the hot wall during one half-cycle is equal to the heat flowing back during the next half, and it is of interest to ascertain how the heat flow varies with the thickness of the plate. On the assumption that the temperature at the surface $z=b$ changes according to the law $V\cos 2\pi ft$ or $V\cos pt$, f being the number of cycles per second, the temperature distribution is given by the relation (1, p. 212) in which $\mu=\sqrt{p/2\varkappa}$

$$v = \frac{V}{2}\left[\frac{\sin\mu(1+i)z}{\sin\mu(1+i)b}\epsilon^{-ipt} + \frac{\sin\mu(1-i)z}{\sin\mu(1-i)b}\epsilon^{+ipt}\right] +$$

$$\frac{2V}{b}\sum_{n=1}^{\infty}(-1)^n \sin n\frac{\pi}{b}z \quad \frac{n^2\frac{\pi^2}{b^2}}{n^4\frac{\pi^4}{b^4}+\frac{f^2}{\varkappa^2}}\epsilon^{-n^2\frac{\pi^2}{b^2}\varkappa t}.$$

The flow of heat $-k dv/dz$ through unit area of the section at z and time t is therefore represented by the formula

$$C = -\frac{\mu k V}{2}\left[\frac{(1+i)\cos\mu(1+i)z}{\sin\mu(1+i)b}\epsilon^{-ipt} + \frac{(1-i)\cos\mu(1-i)z}{\sin\mu(1-i)b}\epsilon^{+ipt}\right] -$$

$$\frac{2kV}{b}\sum_{1}^{\infty}(-1)^n\cos n\frac{\pi}{b}z \quad \frac{\frac{\pi^2}{b^2}}{\frac{\pi^2}{b^4}+\frac{4f^2}{n^4\varkappa^2}}\epsilon^{-n^2\frac{\pi^2}{b^2}\varkappa t}.$$

For the more common insulating materials $\varkappa$ varies from 5×10^{-4} to 5×10^{-3}, and f may vary from 10^{-5} cycles per sec. that is, about one cycle per day, to 100 or more cycles per sec. As b will usually amount to a few cm. at least the fraction in the second term is nearly unity for very slow changes; for frequencies above one cycle per sec. it is no more than a negligible fraction. The whole sum is thus smaller than $2k\frac{V}{b}\left(\theta(z/b,q)-1\right)$, and will vanish with time at about the same rate as the steady state is established in the case of the "plate" method. After about 10 min. only the first term contributes to the transfer of heat in the slab. In this stage the flow has become simply periodic so that the exchange of heat, H, per half-cycle is readily computed for the two boundary planes by integrating over the interval 0 to π/p and π/p to $2\pi/p$.

$$H = -\frac{i\mu k V}{2p}\left(\frac{(1+i)\cos\mu(1+i)z}{\sin\mu(1+i)b}\epsilon^{-ipt} - \frac{(1-i)\cos\mu(1-i)z}{\sin\mu(1-i)b}\epsilon^{+ipt}\right)_{o}^{\pi/p}.$$

This gives for the amount of heat entering or leaving each half-cycle at the side of the variable temperature the following expression

$$H_b = \pm 2\frac{\mu}{p}kV\frac{\sin h2\mu b - \sin 2\mu b}{\cos h2\mu b - \cos 2\mu b}.$$

As the thickness of the slab considered becomes greater, the exchange of heat tends towards the constant value $\pm k V\sqrt{1/\pi\varkappa f}$ in agreement with the formula given by the simpler theory developed for this special case (Table II).

TABLE II

CHANGE OF HEAT TRANSFER PER HALF-CYCLE WITH b

$2\mu b =$	$\pi/4$	$\pi/2$	$3\pi/4$	π	$5\pi/4$	$3\pi/2$	$7\pi/4$	2π
$H_b =$	0.260	0.690	0.75	0.92	1.0	1.02	1.01	1.00
$H_o =$	−0.128	−0.134	−0.34	−0.398	−0.36	−0.13		−0.08

On the other hand the amount of heat flowing during each half-cycle into, or out from, the cold plane is given by the equation

$$H_0 = \pm 2\frac{\mu}{p} k V \frac{\cos \mu b \sin h\mu b - \sin \mu b \cos h\mu b}{(\cos \mu b \sin h\mu b)^2 + (\sin \mu b \cos h\mu b)^2}.$$

It has its highest value for small thicknesses. The difference, finally, between H_b and H_0 represents the capacity of storing heat during one half-cycle and releasing it during the next half.

Other periodic changes may be treated by combining a series of waves. The solution as given applies only to those cases in which the temperature of the boundary planes themselves undergoes fluctuations; when instead, the temperature of the surrounding air varies up and down, the contact or surface resistance which is offered to the heat flow by the surface of discontinuity must be taken into account. Its effect on heat transference through the slab will be most marked in the case of good conductors. The expression giving the heat flow also represents the distortion which an alternating electric current suffers in passing through a long transmission line or cable grounded at the farther end. It is necessary only to replace κ by $1/r_1c_1$, where r_1 is the resistance, c_1 the capacity per unit length.

Acknowledgment

The author is indebted to Mr. F. E. Lathe, who proposed the problem, for his interest and suggestions.

References

1. CARSLAW, H. S. Theory of the conduction of heat. 2nd ed., 1921.
2. GELIUS, S. Z. Ver. deut. Ing. 75: 369-370. 1931.
3. HAYASHI, KEIICHI, Tafeln der Bessel, Theta und anderer Funktionen. 1930.
4. HENCKY, K. Die Waermeverluste durch ebene Waende. 1921.

A CONVENIENT MECHANICAL MEANS OF WINDING QUARTZ SPIRALS[1]

By J. S. Tapp[2]

Abstract

A mechanical device has been constructed for the automatic winding of quartz spirals with any desired pitch. The resultant spirals are compact, accurate and uniform, and are produced with a minimum of personal attention. A study was made of the relationship between the sensitivity and the diameter of the fibre employed.

The machine itself is inexpensive and involves no complicated parts. About 50 successful spirals have been prepared in the manner recorded.

Preparation of Fibres

The most essential prerequisite was a uniform quartz fibre of the proper thickness. The quartz could best be drawn out by a falling weight acting through a system of strings and pulleys to give a horizontal pull. A foot-operated trigger held the weight in check and when released simultaneously removed the flame from the quartz. Fibres about 9 or 10 ft. long were successfully produced in this way and a little practice soon enabled the operator to predetermine, with considerable accuracy, the resultant diameter of the fibre by an adjustment of the amount of quartz heated. Since only 4 or 5 ft. of quartz fibre was necessary for a satisfactory spiral the unsuitable portions of the original 9 or 10 ft. could be discarded and in this way a sufficient length of the proper size could almost invariably be obtained.

The Winding

This operation, when performed by hand, required about 45 or 50 min. of very close attention and, even at best, the spiral obtained was unevenly spaced.

To dispense with this tedious process a machine was designed and constructed from "Erector" parts to perform the same task more easily and to produce uniform coils. The device automatically revolved the rod around which the fibre was being wound and at the same time advanced the rod horizontally so as to give the resultant spiral a uniform and adjustable pitch. Furthermore, there was maintained on the fibre a friction tension which could be conveniently altered during the course of the winding if desired.

The essential parts of the machine are shown in the accompanying sketch.

The power was supplied by a small six-volt d.c. high-speed electric motor, *A*, which revolved at about 3200 r.p.m. A pinion, *B*, on the motor shaft engaged the flat gear, *C*, which in turn through a pulley and belt caused the shaft, *E*, to revolve with a speed reduction of 9 to 1 relative to the motor. This shaft, by means of a worm gear, *H*, further reduced the speed (25 times) and conveyed the power to shaft *L* which, through a pinion and large flat gear, caused the chuck, *R*, to revolve at about 4 r.p.m. A 7 by $\frac{1}{4}$ in. carbon rod, *S*, was held

[1] *Manuscript received April 4, 1932.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada.

[2] *Demonstrator in Physical Chemistry, McGill University.*

in the chuck and kept in line by a free bearing, T, at the opposite end. Directly behind the large gear and turning with the chuck shaft was a three-inch flat steel disk, F, one face of which was covered with a sheet of thin cardboard. Against this disk was pressed a three-inch wheel with a narrow friction rim, D, mounted on a shaft at right angles to the one previously mentioned. By means of a pinion and crown gear (3-1) the movement of this shaft was communicated

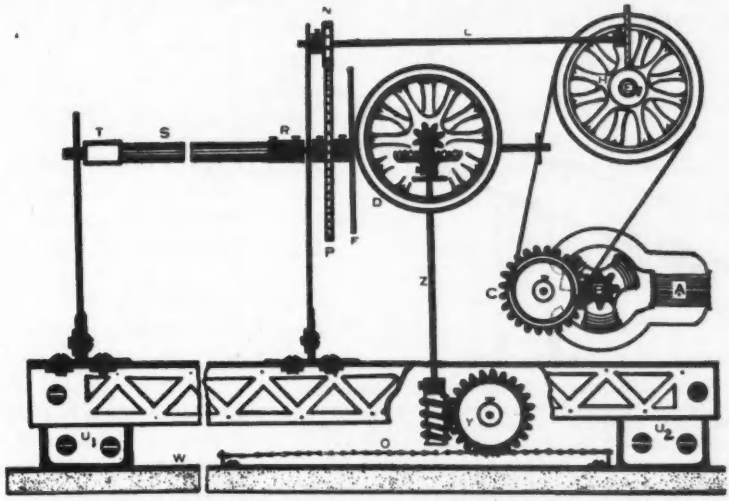


FIG. 1. *Diagram of apparatus built for the winding of the quartz spirals. (Length, about 18 in.; height, about 10 in.)*

to a vertical shaft, Z, extending down through the platform of the machine. This shaft had a worm gear attached at its lower end which meshed with a flat gear, Y, (25-1), mounted on a short shaft placed at right angles to the longitudinal axis of the machine. The lower part of this same gear meshed with a chain which was securely fastened level with the base and parallel with the longitudinal axis of the machine. As the chuck revolved, the system of gears just described caused the gear in contact with the chain to advance along its length at a speed determined by the radial position of the friction drive, and thereby carry along the whole machine at a uniform but adjustable rate of speed. (U_1 and U_2 are steel skids which support the machine and slide in a grooved track W.)

In Fig. 2 is shown the apparatus used for heating the fibre and applying tension. A is an air-blast gas burner, B the revolving carbon rod on which the spiral is wound, C_1 and C_2 are two plates with narrow vertical slits through which the fibre H passes. D is the friction plate bearing against a similar one beneath, and E is the tension adjusting screw. N is a pivot around which the upper part of the tension plate may be revolved to allow of convenient threading of the fibre. R is another pivot which permits the elevation or partial rotation

of the entire guide so as to assure correct alignment at all times. *Y* is a firm upright which is securely fastened to the wooden base and supports the guide and tension mechanism.

The heat required to soften the quartz thread was supplied by the air-blast gas burner mounted on a retort stand and held in position by a clamp. The exact position and intensity of this flame required a great deal of study and trial before it was correctly placed. In the first place it must be of sufficient intensity to soften, and yet not appreciably weaken, the fibre, for in the latter case the tension would cause the fibre to thin out and snap. A very hot flame directed at not quite the right angle was also useless, because once the quartz fibre touched the carbon rod no amount of heat would then cause it to become permanently bent. The best results were obtained when the peak of the blue inner cone of the flame just touched the fibre about 2 mm. in advance of the carbon rod, and when the axis of the flame, if produced, would pass down the centre of the incoming fibre. Many other arrangements were tried but none met with as good success as the one just described.

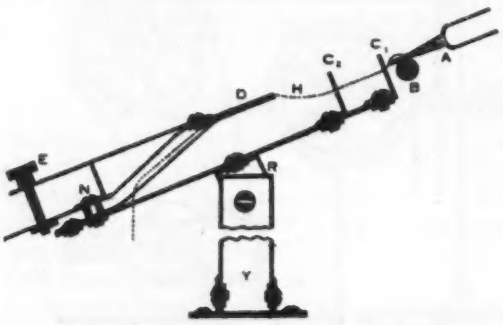


FIG. 2. *Diagram of the tension and guide device, mounted on the same base with the winding mechanism and placed at right angles to the plane of Fig. 1. in a position opposite the carbon rod (S).*

Since the amount of extension caused by any given force is directly proportional to the number of turns in the spiral and also to the diameter of the spiral, it would be advantageous to have as many turns as possible, and for the sake of compactness, as close together as possible. Increasing the diameter of the spiral proportionately reduces the number of turns that can be obtained from a specified length of quartz. In the author's opinion, the spiral with the small diameter and more numerous turns has an advantage in all cases, and certainly has in investigations carried out under high pressures where smallness of the container is a safety factor. The machine was capable of adjustment to give spirals with from 20 to 50 turns per inch as desired. The optimum was found to be about 42 or 43, any more than that resulted in occasional overlaps which were ruinous.

The spiral when finished was slipped off the carbon rod and neat rings formed at each end.

Calibration

The process of calibration consisted merely of suspending the spiral from some solid support and measuring with a cathetometer the length between the upper tip of the top ring and the lower tip of the bottom ring. This length

for any spiral was termed its "normal length". Small calibrated metal weights were then suspended from the bottom and the length measured as before.

Sensitivity

The weight in grams divided by the extension in mm. was termed the "sensitivity". The sensitivity, when multiplied by the fraction of a millimeter to which the cathetometer was capable of measuring accurately ($\frac{1}{20}$ mm. in this case) gave the "limit of detection" for the spiral in question.

The "maximum load" was that weight which caused an extension of two and one-half times the normal length.

Several experiments were carried out with spirals made of fibres of different diameters and it was found that, for a spiral of 80-90 turns, the relationship shown in Table I held approximately. All spirals were of the same diameter, about $\frac{1}{4}$ in.

TABLE I

RELATIONSHIP BETWEEN DIAMETER OF FIBRE AND SENSITIVITY OF SPIRAL (DIAMETER OF SPIRAL, ABOUT $\frac{1}{4}$ IN.)

Diameter of fibre, mm.	0.13–0.15	0.10 –0.11	0.09 –0.10	0.08 –0.09
Sensitivity, gm. per mm.	<0.03	0.011–0.018	0.0072–0.0080	0.0040–0.0060

References

1. McBAIN, J. W. and BAKER, A. M. J. Am. Chem. Soc. 48: 690-695. 1926.
2. PIDGEON, L. M. and MAASS, O. J. Am. Chem. Soc. 52: 1053-1068. 1930.

THE ELECTRICAL CONDUCTIVITY OF AQUEOUS SOLUTIONS OF HYDROGEN SULPHIDE AND THE STATE OF THE DISSOLVED GAS[1]

By R. H. Wright[2] and O. Maass[3]

Abstract

This paper is the last of three dealing with the equilibria between hydrogen sulphide and water, and is a continuation of a series of researches designed to investigate the equilibria existing in gaseous aqueous systems.

Electrical conductivities of aqueous solutions of hydrogen sulphide have been measured between 5° and 60°C. The results lead to the conclusion that hydrogen sulphide resembles certain other gaseous solutes and forms with water a complex which undergoes electrolytic dissociation. The constant k of the Ostwald dilution law therefore appears to be an apparent, rather than a real, dissociation constant.

The complete analysis of the equilibria involved and the evaluation of the constants must depend on accurate measurements at low concentrations, which are not yet completed.

Introduction

The state of hydrogen sulphide dissolved in water has hitherto been known only from the scattered observations of a number of observers. It has been the object of the work described in this and two preceding papers (10, 11) to secure an homogeneous body of information from which the nature of aqueous solutions of hydrogen sulphide could be deduced. To this end, the partition of hydrogen sulphide between the vapor and aqueous phases has been determined and the conductivities of the solutions have been measured. This paper is devoted to the latter of these measurements and the preliminary theoretical consideration of the problem as a whole.

The object of the partition experiments was to determine the solubility curves in such a way as to eliminate all sources of deviation from the ideal laws not arising in the liquid itself. For instance, an apparent departure from Henry's law (regarded as a particular case of the partition law) might easily be caused by failure of the hydrogen sulphide in the vapor to obey the simple gas law*. Any departure, therefore, from the partition law after allowing for these extraneous effects may tentatively be ascribed to conditions in the liquid such as association, dissociation, hydration, etc.

The electrolytic dissociation of hydrogen sulphide is known to take place in two steps but, as it has been well shown (2, 5, 6) that the constant of secondary dissociation is vanishingly small, in this work hydrogen sulphide will be treated as a monobasic acid.

*That allowance for this factor is indeed necessary is shown by the results in the previous paper (11), in Fig. 5 of which the solid lines show the actual variation of the concentration of the solution with concentration of hydrogen sulphide in the vapor, whereas the dotted lines represent the curves obtained when the vapor was treated as an ideal gas.

[1] *Manuscript received April 8, 1932.*

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada. Constructed from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry, McGill University.

[2] *Assistant Professor of Chemistry, University of New Brunswick, Fredericton, New Brunswick, and holder, at the time, of a bursary and studentship under the National Research Council of Canada.*

[3] *Professor of Physical Chemistry, McGill University.*

The experimental data for the electrical conductivity submitted in this paper are the first that have been published having any claim to comprehensiveness or precision.

Determination of Electrical Conductivity

Experimental Method

Previous attempts to measure the electrical conductivity of hydrogen sulphide solutions have been hampered by experimental difficulties arising from polarization of unplatinized electrodes and occlusion of hydrogen sulphide by platinum black. Control and measurement of the concentration have also been difficult (1, 9).

By adapting the sealed cell procedure described in the preceding paper (11), the latter of these difficulties has been overcome, and the problem of polarization has been avoided altogether by using the static method of conductivity measurement. This method is not new but it has lately been improved in these laboratories and elsewhere and seems quite satisfactory.

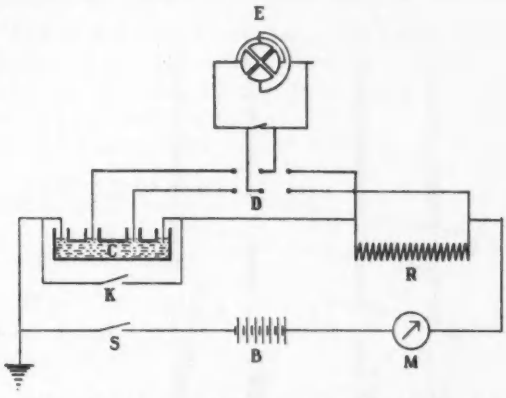


FIG. 1. *Diagram showing arrangement of apparatus for the electrical conductivity determinations.*

The principle of the method is very simple. If two resistances R_1 and R_2 be connected in series and a current passed through the circuit, then if E_1 is the potential across R_1, and E_2 the potential across R_2,

$$\frac{E_1}{E_2} = \frac{R_1}{R_2}.$$

Fig. 1 shows the application of this principle to the measurement of electrical conductivities. The conductivity cell, C, was connected in series with a resistance, R, milliammeter, M, battery of dry cells, B, and a switch, S. The cell was provided with two exploring or "secondary" electrodes which lay between the primary ones.

By means of the double pole, double throw switch, D, the secondary electrodes or, alternatively, the resistance, R, could be connected to the quadrants of a Dolezalek electrometer, E. Since the deflection of the electrometer was related to the potential difference of opposite pairs of quadrants, then, from the ratio of the deflections the ratio of potential fall between the exploring electrodes to the potential fall across the known resistance could be obtained. Since the current was the same through both, this ratio was also the ratio of the resistances. The absolute values of the potentials and of the primary current were within limits immaterial, so that the resistivity of the solution was found in terms of two electrometer deflections and a known resistance.

Since, however, the electrometer deflections were for various reasons not strictly proportional to the applied potentials, the electrometer was first calibrated by connecting a number of combinations of standard cells to the quadrants and plotting a curve of potential against deflection.

The usual precautions of insulation, shielding, etc., were taken in setting up the apparatus.*

The conductivity cell used is shown in Fig. 2. It was made of Pyrex glass and the electrodes were of thin platinum ribbon, unplatinized and adhering closely to solid glass supports as shown. The secondary electrodes, *B* and *C*, had a very much smaller surface than the primary and consisted simply of small platinum tips projecting into the side arms, the entire side arm constituting the exploring electrode.

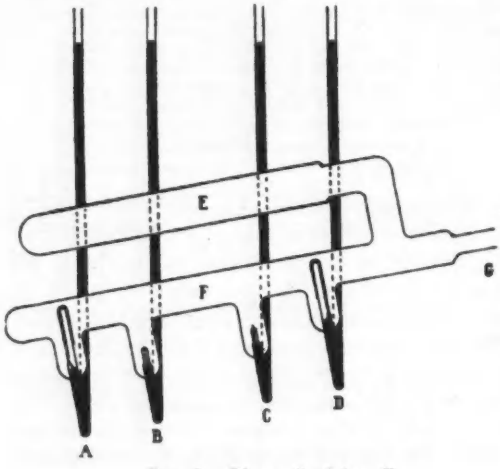


FIG. 2. *The conductivity cell.*

The cell was mounted on a mechanical rocker placed in a thermostat. The cell contents could be thoroughly stirred by rocking the cell back and forth between readings. The electrometer connections to the mercury wells were made through flexible wires and were not removed during the rocking.

A cell constant was determined using 0.02 *N* and 0.01 *N* KCl, the specific conductivities of which were taken as 0.002765 and 0.001413 respectively, at 25° C. (7, p. 213). The water correction was obtained from a blank run.

The procedure in filling the cell was similar to that described in the previous paper (11). The water was not, however, run directly into the conductivity cell from the weight pipette, but into a bulb temporarily sealed to the apparatus. In this bulb it was freed from dissolved air by freezing and melting *in vacuo* and was then distilled into *E*, Fig. 2. The hydrogen sulphide was purified and measured as previously described, and condensed in *F* with liquid air while the water in *E* was frozen with solid CO_2. The cell was then sealed off at *G* and the conductivity of the resulting solution measured at various temperatures. At the conclusion of the measurements the cell was opened and its volume found by filling with distilled water and weighing.

*It is usual to ground one pair of quadrants, but it was found in this work that better results were obtained by grounding a point in the primary circuit instead.

Results

The concentration of the solution at each temperature was found as shown in the following specimen calculation. As the partition coefficient of hydrogen sulphide between liquid and vapor varies with the pressure, an approximate calculation was first made showing roughly the pressure in the cell. The appropriate value of the distribution coefficient was then selected from the data of the previous paper (11, Fig. 6).

Specimen Calculation

Temperature, 20° C.; wt. of H_2S, 0.7439 gm.; wt. of H_2O, 42.38 gm.; vol. of water, 42.49 cc.; approximate pressure, 2100 mm.; approx. wt. of H_2S in solution, 0.460 gm.; increment of volume due to dissolved gas (from mixture rule), 0.54 cc.; volume of solution, 43.03 cc.; volume of the cell, 113.08 cc.; volume of the vapor, 70.05 cc.; partition coefficient D (20° C. and 2100 mm.), 2.67.

$$\text{Weight of } H_2S \text{ in solution} = \frac{D \times (\text{vol. of soln.}) \times (\text{total wt. } H_2S)}{(\text{vol. of vapor}) + D \times (\text{vol. of soln.})}$$

$$= \frac{2.67 \times 43.03 \times 0.7439}{70.05 + 2.67 \times 43.03}$$

$$= 0.462 \text{ gm.}$$

$$\text{Molarity of solution,} \quad \frac{0.462 \times 1000}{34.08 \times 43.03}$$

$$= 0.0316.$$

From the scale readings, electrometer calibration curve and cell constant, the specific conductivity was obtained at a number of temperatures, and values at other temperatures were interpolated. To obtain the degree of dissociation, the limiting equivalent conductivity at infinite dilution was calculated from the data of Jellinek and Czerwinski (4) who measured the conductivity of NaSH solutions at 0°, 18° and 25°C. The ion conductances of Na^+ and H^+ were taken from the International Critical Tables (3). The limiting conductance of hydrogen sulphide at other temperatures was obtained by interpolation. These conductances are given in Table I.

TABLE I

LIMITING EQUIVALENT CONDUCTANCE OF HYDROGEN SULPHIDE

Temp., °C.	0	5	10	15	18	20	25	30	40	50	60
Λ	269	299	328	356	372	385	414	442	499	556	613

The constant, k, of the Ostwald dilution law (*i.e.*, the apparent dissociation constant) was calculated from the formula,

$$k = \frac{M\left(\frac{\Lambda_v}{\Lambda_\infty}\right)^2}{1 - \frac{\Lambda_v}{\Lambda_\infty}}$$

where, M is the molarity of the solution, Λ_v the equivalent conductivity at concentration M, and Λ_∞ the equivalent conductivity at infinite dilution.

The results are summarized for each temperature in Table II, and in Table III values of the apparent dissociation constant are collected and compared with those of other authors.

TABLE II

EXPERIMENTAL RESULTS

Total pressure	Partial pressure	Molarity	Specific cond. $\times 10^6$	$\frac{\Lambda_v}{\Lambda_\infty} \times 10^3$	$k \times 10^6$
At 5°C.					
607	601	0.141	2.44	0.578	4.72
903	897	.208	2.91	.479	4.77
1181	1175	.270	3.35	.415	4.65
At 10°C.					
684	675	.135	2.95	.665	5.99
1011	1002	.199	3.58	.547	5.98
1321	1312	.259	4.12	.485	6.09
1758	1749	.343	4.56	.406	5.64
At 15°C.					
758	745	.129	3.49	.759	7.45
1117	1104	.190	4.28	.631	7.59
1459	1446	.248	4.92	.557	7.70
1940	1927	.329	5.45	.466	7.13
At 20°C.					
832	815	.124	4.04	.841	8.75
1224	1207	.182	4.98	.710	9.19
1611	1594	.240	5.72	.619	9.20
2125	2108	.315	6.38	.526	8.71
At 25°C.					
907	883	.118	4.64	.948	10.6
1332	1308	.174	5.72	.794	11.0
1741	1717	.228	6.55	.694	11.0
2308	2284	.302	7.33	.586	10.4
At 30°C.					
982	950	.113	5.24	1.05	12.4
1436	1404	.167	6.48	.879	12.9
1879	1847	.218	7.41	.767	12.9
2480	2448	.289	8.31	.650	12.2
At 40°C.					
1132	1077	.104	6.48	1.24	16.2
1639	1584	.153	8.02	1.05	16.9
2147	2092	.202	9.15	.910	16.7
2829	2774	.267	10.3	.771	15.9
At 50°C.					
1282	1190	.097	7.73	1.44	20.0
1849	1757	.142	9.53	1.21	20.8
2421	2329	.867	10.9	1.05	20.5
3163	3071	.245	12.3	.898	19.8
At 60°C.					
1444	1295	.091	9.00	1.62	23.8
2060	1911	.133	11.0	1.36	24.4
2689	2540	.175	12.6	1.17	24.2
3551	3405	.232	14.2	1.00	23.2

TABLE III

SUMMARY OF DILUTION LAW CONSTANTS

Temp., °C.	5	10	15	20	25	30	40	50	60
k, mean value $\times 10^8$	4.71	5.74	7.47	8.96	10.8	12.6	16.4	20.3	23.9

Values from the literature

Observer	Jellinek and Czerwinski (4)	Auerbach (1)	Walker and Cormack (9)
Temp., °C.	0	18	18
k	1×10^{-8}	9.1×10^{-8}	5.7×10^{-8}

Discussion

The most striking feature of the experimental results is the regular and marked increase in the dilution law constant, k, with rise in temperature. Applying the equation

$$\frac{d \ln K}{dT} = \frac{-q}{RT^2},$$

$+q$ will signify the heat evolved in the reaction

$$H_2S \longrightarrow H^+ + SH^- + q.$$

The ordinary method of integration can be applied using the formula,

$$\ln \frac{k_2}{k_1} = \frac{q}{R} - \left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

Taking values of k from Table III, it is found that integrating from 5° to 25°C. gives $+q = -6800$ cal., whereas integrating from 30° to 60°C. gives $+q = -4300$ cal.

So great a change in q can hardly be explained by Kirchoff's theorem in terms of changes in the heat capacities of the ions or the dissolved hydrogen sulphide, and another explanation must be sought.

By assuming that when hydrogen sulphide dissolves in water, the solvent and solute unite to form a complex which then undergoes electrolytic dissociation, the above result becomes intelligible. The quantity q will then depend on two independent quantities, Q_1 the heat evolved in forming the complex from hydrogen sulphide and water, and Q_2 the heat evolved in the ionization of this complex. If Q_2 has a negative value, *i.e.*, if the dissociation of the complex is attended by the absorption of heat (which is to be expected from the similarity of hydrogen sulphide and water, an increase in the extent of ionization would be expected with rise in temperature. This tendency would, however, be opposed by the decrease in the dielectric constant of water, and in any case the degree of ionization seldom varies extensively with temperature.

The observed increase in k may also be explained in another way. Supposing Q_1 to have a negative value, *i.e.*, that the H_2S-H_2O complex is endothermic, then a rise in temperature would favor its formation and would therefore produce an increase in the number of ions over and above any increase due to a change in the ionization constant of the complex.

Furthermore, it is evident that $-q$ is the net heat evolved when (a) the ions combine to form the complex and (b) when a part of the complex then dissociates into free hydrogen sulphide and water. Assuming an endothermic complex, the process (b) will be relatively more important at low than at high temperatures in so far as it contributes to the net heat evolution q. The marked decrease in q at higher temperatures is therefore readily explained by the hypothesis of an endothermic complex.

The system may now be provisionally formulated in the following way (secondary dissociation being neglected).

$$H_2S \text{ (in vapor)} \rightleftharpoons H_2S \text{ (in solution)}.$$
$$H_2S \text{ (in soln.)} + nH_2O \rightleftharpoons H_2S.nH_2O + Q_1.$$
$$H_2S.nH_2O \rightleftharpoons H^+ + SH^-.nH_2O + Q_2.$$

Corresponding to each equilibrium there will be an equation:

$$\frac{[H_2S]_{\text{soln.}}}{[H_2S]_{\text{vap.}}} = h, \quad \frac{[H_2S]\,[H_2O]^n}{[H_2S.nH_2O]} = K_1, \quad \frac{[H_2S.nH_2O]}{[H^+]\,[SH^-.nH_2O]} = K_2.$$

It is evident that the system is now analogous to the systems treated by Maass and Morgan (8), *viz.*, sulphur dioxide and water, carbon dioxide and water, and ammonia and water. There is however an important difference. In all the systems treated by these authors, the formula of the complex (H_2SO_3, H_2CO_3, and NH_4OH) could be inferred from the composition of the salts formed, whereas there is no such clue to the value to be assigned to n in the equations above.

Maass and Morgan found that measurements at high concentrations were necessary for the evaluation of K_1 and K_2 in the systems examined by them. From a consideration of the present problem, it appears that measurements with very low concentrations are also required when n has also to be determined. Since these have not yet been made, this paper can include only a qualitative consideration of the system.

The assumption of a complex such as has been described will also account, in a qualitative way, for the form of the vapor pressure curves of the preceding paper (11, Fig. 5). From the equation,

$$\frac{[H_2S]\,[H_2O]^n}{[H_2S.nH_2O]} = K_1$$

it is evident that as $[H_2S]$ increases (at constant temperature) $[H_2S.nH_2O]$ will also increase, but relatively more slowly owing to the diminution in $[H_2O]$. The net result of $[H_2S]$ increasing more rapidly than $[H_2S.nH_2O]$ will be a curvature in the solubility curves of the kind actually displayed by the isotherms of the previous paper (11).

References

1. AUERBACH, F. Z. physik. Chem. 49: 217-223. 1904.
2. AUMÉRAS, M. Compt. rend. 186: 1724-1726. 1928.
3. INTERNATIONAL CRITICAL TABLES, v. 6, McGRAW-HILL. 1929.

4. JELLINEK, K. AND CZERWINSKI, J. Z. physik. Chem. 102: 438-479. 1922.
5. KNOX, J. Z. Elektrochem. 12: 477-481. 1906.
6. KNOX, J. Trans. Faraday Soc. 4: 29-50. 1908.
7. LANDOLT-BÖRNSTEIN. Physikalisch-chemische Tabellen. v. 2. Springer, Berlin. 1923.
8. MORGAN, O. M. and MAASS, O. Can. J. Research, 5: 162-199. 1931.
9. WALKER, J. and CORMACK, W. J. Chem. Soc. 77: 5-21. 1900.
10. WRIGHT, R. H. and MAASS, O. Can. J. Research, 5: 442-447. 1931.
11. WRIGHT, R. H. and MAASS, O. Can. J. Research, 6: 94-101. 1932.

AN EQUATION OF STATE FOR GASES AT LOW DENSITIES[1]

By D. LeB. Cooper[2] and O. Maass[3]

Abstract

An equation of state for gases at low densities is developed, using a new function for the change in viscosity with temperature, also developed herein.

The gas law equation takes the form

$$PV^2+a-RTV-\frac{RTb(1+KT_0)}{1+KT}=0$$

or $V(1+KT)(PV-RT)=\lambda T-a$ where a and b are constants corresponding to those of the Van der Waals' equation, and K is a constant derived from the proposed viscosity function which is, for carbon dioxide,

$$\eta=\sqrt{T}(1+KT)$$

where K is a constant and η is the viscosity at an absolute temperature T.

In the case of carbon dioxide the equation was found to follow density results with an accuracy of from 0.01% to within experimental limits, and the viscosity function was found to agree with Sutherland's (10) results between −78.5 and 20° C.

Comparisons with several other equations of state are made. These show that the new equation is probably more accurate than any other.

An expanded form of the new equation, namely:

$$\frac{M^1}{M_0}=1+\left(a-\frac{RTb_0}{1+KT}\right)\frac{P}{R^2T^2}+2\left(a-\frac{RTb_0}{1+KT}\right)^2\frac{P^2}{R^4T^4}+\text{etc.}$$

permits calculations of the slopes of isothermals for any temperature. Comparisons are made with experimental data.

The expanded form of the equation may be solved for K, giving the expression:

$$\frac{(\theta_1-\theta_2)\ (\theta_3+K)}{(\theta_1-\theta_3)\ (\theta_2+K)}=\frac{\lambda_1-\lambda_2}{\lambda_1-\lambda_3}$$

where $\theta=\frac{1}{T}$ and $\lambda=a-\frac{\xi}{\theta+K}$ and $\xi=Rb_0$, and since the equation enables the calculation of the molecular radius r, the viscosity may be calculated for any temperature and pressure over which the equation holds.

Introduction

The authors (5) have published the results of measurements of the density of carbon dioxide. The accuracy of the results was of the order of 0.01%, approximately 10 times that of previously existing data. The object of this communication is to apply these previously published results to the examination of some equations of state including a new one proposed herein.

The application of the new equation is restricted to gases at low densities. The restriction is intentional and succeeded a consideration of the possibilities of the usefulness of equations of state for deductions concerning molecular phenomena. These considerations are outlined below.

An infinitely dilute gas is usually considered "ideal". More correctly, it approaches the ideal as its density decreases. Increasingly large aberrations follow increasing density. Representation of these aberrations by correction

[1] *Manuscript received April 19, 1932.*
Contribution from the Department of Physical Chemistry, McGill University, Montreal, Canada.

[2] *Holder, at the time, of a fellowship under the National Research Council of Canada.*

[3] *Professor of Physical Chemistry, McGill University.*

terms applied to the ideal gas law equation presupposes at least partly analogous conditions between the actual and the ideal. Representation of high pressure data is complicated by the fact that neither is the term "molecular volume" unique, nor "mean free path" significant. As a consequence it appears to be a reasonable supposition that more pregnant deductions can be made by the use of low density data and equations holding in that region in which partially analogous conditions exist.

The proposed equation is developed by the use of a Van der Waals' (12) molecule. Possibly that developed by Lennard-Jones (8) has the greatest significance compatible with tractability, but with a restriction to the low density region and assumption that the effective molecular radius does not vary within the second order of small quantities, and furthermore that at low densities the attractive field is not appreciably affected by pressure, the use of a simpler Van der Waals' molecule is not only justified but preferable. This is more particularly true in the treatment of gases with large molecular fields and relatively soft molecules.

The degree of conformity of the equation based on these postulates determines whether or not the above assumptions are justified.

Mathematical Development of Equation

Maass and Mennie (9) have shown that the pressure of an ideal gas may be represented by the equation

$$\left(P+\frac{A}{V^2}\right)V=\left(1+\frac{2r}{l}\right)RT, \tag{1.0}$$

where r is the molecular radius, l the mean free path, A a Van der Waals' constant of attraction, and P, V, R and T have their usual significances. If, as postulated above, r and A remain effectively constant, the variation in the deviation (PV-RT) results from changes in l.

The variation in l may be represented as a function of the temperature.

Sutherland's (11) expression incorporated in equation (1.0) yielded the following:

$$PV^2-RTV+A-RTB\left(1+\frac{C}{T}\right)=0, \tag{1.1}$$

where

$$B=\frac{8\sqrt{2}\,\pi r^3 N}{1+\frac{C}{273}}, \tag{1.2}$$

or

$$PV^2-RTV+A-RTB^1=0. \tag{1.3}$$

Maass and Mennie (9) point out that this equation may be transformed into one identical with that of Van der Waals' by a first order approximation, and that in agreement with the fact that Sutherland's function fails at low temperatures, Equation (1.3) fails at temperatures below 0° C.

It was believed that an equation of this type was capable of further development provided a rigid function for variations in l with temperature could be found. The following is offered as a solution.

The mean free path l is related to the viscosity by an equation such that

$$\eta = K_1 mn\chi l, \tag{2.0}$$

where K_1 is an unknown constant. Or, more accurately, since η changes more rapidly than $\sqrt{T}$

$$\eta = K_1 mn\chi l f(T). \tag{2.1}$$

But $$\chi \propto \sqrt{T},$$

therefore $$\eta = K_1 mn\sqrt{T}\, l f(T), \tag{2.2}$$

and the viscosity at 0° C. is $$l_0 = \frac{\psi}{4\sqrt{2}\,\pi r^2 n},$$

where ψ is some constant, and as $l = l_0$ when $\eta = \eta_0$ (assuming as before that the total change in η is caused by a change in l) therefore

$$\eta_0 = \frac{\psi K_2 mn\sqrt{T} f(T)}{4\sqrt{2}\,\pi r^2 n}, \tag{2.3}$$

whence $$\eta = K_3\sqrt{T} f(T), \tag{2.4}$$

where $$K_3 = \frac{\psi K_2 m}{4\sqrt{2}\,\pi r^2} = \text{const.}, \tag{2.4.1}$$

or $$\frac{\eta}{\sqrt{T}} = K_3 f(T). \tag{2.5}$$

The data of Sutherland and Maass (10) was used to plot $\frac{\eta}{\sqrt{T}}$ against T for carbon dioxide and $f(T)$ was found to be a straight line, whence

$$\frac{\eta}{\sqrt{T}} = 1 + KT, \tag{2.6}$$

and we may write $$l = l_0 \frac{(1+KT)}{(1+KT_0)}, \tag{2.7}$$

whence substitution in (1.3) gives

$$\left(P + \frac{a}{V^2}\right) V = RT\left[1 + \frac{2r(1+KT_0)}{l_0(1+KT)}\right], \tag{3.0}$$

where a is a Van der Waals' constant of attraction differing numerically from A (Equation 1.3).

But $$l_0 = \frac{\psi}{4\sqrt{2}\,\pi r^2 n},$$

whence $$\left(P + \frac{a}{V^2}\right) V = RT\left[1 + \frac{8\sqrt{2}\,\pi r^3 n(1+KT_0)}{\psi V(1+KT)}\right], \tag{3.1}$$

or $$PV^2 + a - RTV - \frac{RTb(1+KT_0)}{1+KT} = 0 \tag{3.2}$$

and $$b = \frac{8\sqrt{2}\,\pi r^3 n}{\psi}.$$

Equation (3.2) may be written

$$V(1+KT)(PV - RT) = b_0 T - a + aKT, \tag{3.3}$$

where $$b_0 = b(1+KT_0) = \text{const},$$

or $$V(1+KT)(PV - RT) = \lambda T - a, \tag{3.4}$$

where $$\lambda = b_0 + aK = \text{const.}$$

Equation (3.4) is the one used for comparisons. The constants K and λ may be evaluated easily and the equation tested for rigidity without difficulty, as inspection shows that the left hand term should vary linearly with T. That this is so is seen from Fig. 1, which shows that the equation holds over the measured range with the desired accuracy. The values of λ and a may be determined directly from the line of Fig. 1.

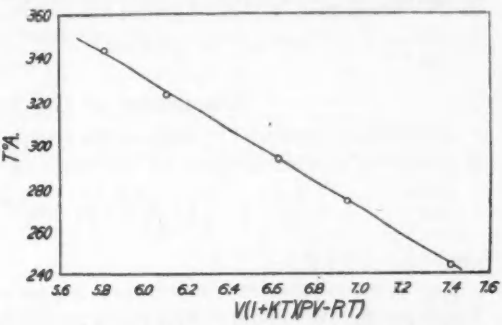


FIG. 1. *The calculated values of $V(1+KT)$ $(PV-RT)$ plotted as a function of T in °A.*

The function may be evaluated as follows. We define a volume, V, such that V represents the actual volume occupied by a theoretical molecular weight of a gas at a corresponding T and P. V is then calculated from the published data from the equation,

$$V = \frac{M_0}{M_1}\frac{RT}{P}. \qquad (A)$$

For purposes of correlation these values are shown in Table I.

TABLE I

APPARENT MOLECULAR WEIGHT AND VOLUME OF A GRAM MOLE OVER A TEMPERATURE RANGE

Temperature ° Abs.	Apparent molecular weight (M_1)	V (observed) litres
243.18	44.422	19.764
273.18	44.295	22.266
293.18	44.232	23.930
323.18	44.167	26.418
343.18	44.138	28.071

The values of RT may be calculated for each temperature and those of $1+KT$ from the viscosity line (Fig. 1) the constants of which are, for carbon dioxide, $1+4.094\times10^{-3}T$. The values of the left hand function lie on a straight line (Fig. 1) the equation for which is

$$\lambda T - a = 1.6167\times10^{-2} - 11.34.$$

The numerical values of the results are shown in Table II, and the exactitude of the equation is demonstrated further by a direct calculation of V shown in comparison with those calculated from several other equations (Table II).

TABLE II

COMPARISON OF RESULTS, V *obs.* AND V *calc.* AT VARIOUS TEMPERATURES; PRESSURE CONSTANT AND EQUAL TO ONE ATMOSPHERE

Temperature ° Abs.	V *obs.*, litres	V_1*, litres	V_2, litres	V_3, litres
243.18	19.764	19.764	19.772	19.952
273.18	22.266	22.266	22.265	22.414
293.18	23.930	23.930	23.930	24.055
323.18	26.418	26.418	26.418	26.517
343.18	28.071	28.071	28.069	28.157

*V_1 = *new equation*; V_2 = *Maass-Mennie equation*; V_3 = *gas law*.

The equation for carbon dioxide is

$$V(1+4.0983\times10^{-3}T)(PV-RT)=1.616\times10^{-2}T-11.34, \tag{3.5}$$

or, written in a form to show minor constants,

$$PV^2+11.34-RTV-RT\frac{0.3596(1+4.0983\times10^{-3}T_0)}{1+4.0983\times10^{-3}T}=0 \tag{3.6}$$

Discussion of the Equation

The equation may be written in the form of an isothermal by substitution of equation (A) and expansion by the binomial theorem. Then,

$$\frac{M^1}{M_0}=1+\left(a-\frac{RTb_0}{1+KT}\right)P+2\left(a-\frac{RTb_0}{1+KT}\right)^2P^2+\ldots, \tag{4.0}$$

where $b_0=b(1+KT_0)$.

The slopes of the isothermals may be calculated from the coefficient of P. These are shown compared with those determined experimentally in Table III.

TABLE III

SLOPES OF LOW PRESSURE ISOTHERMALS

Temperature, ° Abs.	u_1 (observed)	u_2 (calculated)
243.18	0.418	0.413
273.18	0.291	0.288
293.18	0.228	0.229
323.18	0.163	0.164
343.18	0.134	0.135

A variation of 0.01% in the highest molecular weight on any isothermal results in a change of slope of 18%. The calculated values are well within the limits of error. The coefficient of P^2 allows for curvature of the isothermals. It becomes effective at five atmospheres to the extent of 0.01%.

Following are similar expansions of the equations of Maass and Mennie, and Van der Waals, shown for comparison:

Maass and Mennie,

$$\frac{M^1}{M_0}=1+\left(\frac{A-RTB^1}{R^2T^2}\right)P+2\left(\frac{A-RTB^1}{R^2T^2}\right)^2P^2+\ldots \text{ etc.}$$

Van der Waals',

$$\frac{M^1}{M_0}=1-\frac{\alpha-RT\beta}{R^2T^2}P+\ldots\ldots\ldots \text{ etc.}$$

A second method of treatment of the expanded form (4.0) will be discussed later.

Comparison of Equations

Table II and succeeding tables serve to compare the several equations.

TABLE IV

COMPARISON OF RESULTS FROM BRIDGEMAN'S EQUATION FOR AN ISOSTERE AT $V=23.930$ l.

Temp.	*P obs.*	*P calc.*
243.18	0.82730	0.82664
273.18	0.93098	0.93046
293.18	1.0000	0.99970
323.18	1.1035	1.1032
343.18	1.1724	1.1723

Table II shows the calculated volume V compared with those determined experimentally. The values of the Maass-Mennie equation were calculated using their method with constants derived from the published results of the authors. The discrepancy at −30° C. is well outside the limits of error.

Table IV shows comparisons with Bridgeman's equation for carbon dioxide, calculated in the form of an isobar. At the lower tem-

peratures the deviations are greater than experimental errors.

TABLE V

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM VAN DER WAALS' EQUATION USING DIFFERENT VALUES FOR THE CONSTANTS α AND β

(1)	(2)	(3)	(4)	(5)	(6)
		α			
		4.208	7.06	7.56	4.208
Temp., ° Abs.	*P. obs.*	β			
		0.050	0.166	0.188	0.0712
		P. calc.			
243.18	1.0000	1.0013	1.0000	1.0003	1.0024
273.18	1.0000	1.0005	1.0000	0.9999	1.0014
293.18	(1.0000)	(1.0000)	(1.0000)	(1.0000)	1.0009
323.18	1.0000	0.9996	1.0000	1.0001	1.0004
343.18	1.0000	0.9995	1.0000	1.0003	1.0004

Table V requires further discussion. Attempts have been made to calculate the constancy of Van der Waals' a and b, written here, α and β. Algebraically they are unique, and hitherto it has been impossible to detect differences between calculated and experimental values even with considerable differences in the values of the constants used. The more accurate results show that a 7% variation in α causes a noticeable difference at the extreme temperatures even when the volumes are calculated using a corresponding β.

The values of α and β were obtained by a simultaneous solution of Van der Waals' equation using the authors' results: $\alpha = 7.06$; $\beta = 0.166$. Pressures calculated from these values follow the experimental results (column 4). Those calculated (column 6) from the best representative values of the constants based on the results of Amagat (1, p.109) and Andrews (2) and quoted by Jellinek (7, p. 632) show discrepancies varying from 0.2% at low temperatures to 0.03% at the highest. The figures of column 3 were calculated by substitution of the best representative value of α and calculation with a corresponding β.

The results in Table V show that a change in the constants of Van der Waals' equation makes it inapplicable to calculations of the highest accuracy.

Further comparison of Equations (1.3), (3.2) and Van der Waals' is made possible by the fact that the equations are similar when

$$RTB^1 = PV\beta - \frac{\alpha\beta}{V} = \frac{Rb_0T}{1+KT},$$

and, with the first order approximation that $PV = RT$,

$$RTB^1 = RT\beta - \frac{\alpha\beta}{V} = \frac{Rb_0T}{1+KT}.$$

The term $\frac{\alpha\beta}{V}$ affects the results to $\frac{1}{6000}$ and neglecting this,

$$B^1 = \beta = \frac{b_0}{1+KT},$$

or at 0° C.

$$B^1 = \beta = b.$$

TABLE VI
COMPARISON OF *V obs.* AND *V calc.* AT HIGHER PRESSURES

Pressure, obs.	Pressure, (Van der Waals' equation)	Pressure (new equation)
12.01	12.12	12.012
13.22	13.35	13.197
14.68	14.86	14.663
20.01	20.74	19.945
34.49	30.86	33.297

This indicates that at all temperatures other than 0° C. the proposed equation demands a variable, and the others a constant correction factor.

Table VI shows the range over which the new equation holds compared to that of Van der Waals'. The values for the latter were calculated by use of constants obtained from data of the authors. The constants for the proposed equation were obtained, as explained, by a process yielding unique values, for if the value of K be changed 100%, *i.e.*, be placed equal to zero, calculated and experimental values do not agree as is shown in Table VII.

TABLE VII
SHOWING EFFECT OF A CHANGE IN K ON AGREEMENT BETWEEN OBSERVED AND CALCULATED PRESSURES

Temp., ° Abs.	Obs. press.	Calculated pressure	
		$K=0$	$K=4.50$
243.18	1.0000	0.99884	1.0000
343.18	1.0000	1.00150	0.9999

The forms of the equations allow another differentiation. The new equation permits calculations of the slopes of the isothermals as shown above, but Van der Waals' equation has no like application due to the substitution of PV by RT.

Comparison with the equation of Bridgeman (4) is more difficult on account of the relatively large number of semi-empirical constants therein. Table IV indicates that while somewhat similar in form, Bridgeman's equation fails at low temperatures and pressures. At higher temperatures and pressures the agreement is satisfactory.

A more apparent difference between the three equations first mentioned may be detected by writing them in the form of isosteres, whence, for Maass and Mennie, and Van der Waals' we have

$$P=BT-A,$$

and for the recently proposed equation,

$$P=B_1T+\frac{C_1}{1+KT}-a.$$

The first two demand straight isosteres, the latter allows for a curvature. In this respect the new equation probably represents the facts to a greater degree of exactness since isosteres are known to possess a curvature at higher pressures. No curvature was detected in the isothermals, hence no value of C_1 can be calculated. An upper limit was found to be of the order of 1×10^{-4}.

Further Applications of the Proposed Equation

Among others the equation lends itself to two further applications, namely, the calculation of the molecular radius, r, and the viscosity constant K, as defined by Equation (2.6). A knowledge of r permits the calculation of the

viscosity of the gas under examination at 0° C., which value, substituted in Equation (2.6), permits, with a knowledge of K (also calculated from gas law relationships by use of the new equation), a calculation of the viscosity at any temperature over which the equation holds. In so far as the second application is concerned this is the first time that the calculation of viscosities at different temperatures has been possible from PVT results only.

The Molecular Radius

The calculation of the molecular radius may be carried out as follows:

From equation (3.1)

$$PV^2+a-RTV-\frac{RTb(1+KT_0)}{\psi(1+KT)}=0$$

where $b=8\sqrt{2}\,\pi r^3 n,$

therefore $b=6\sqrt{2}\,V_0$, where V_0 is the total volume of the molecules; ψ is a correction factor. Using Jean's calculation of ψ, we have

$$PV^2+a-RTV-\frac{6\sqrt{2}\,V_0(1+KT_0)}{1.382(1+KT)}=0,$$

from which $r=2.28\times10^{-8}$ cm., the calculated viscosity at 0° C. of 0.0001353 differing from the experimental value of 0.0001354 by 0.15%.

The Viscosity Constant

The second application, namely, the calculation of the viscosity constant K from PVT data, may be carried out as follows.

From equation (4.0) we have

$$\frac{M^1}{M_0}=1+\left(\frac{a-\dfrac{RTb_0}{1+KT}}{R^2T^2}\right)P, \tag{6.0}$$

but $M^1=M_0+uP,$

where u is a constant

therefore $$\frac{M^1}{M_0}=1+\frac{u}{M_0}P, \tag{6.1}$$

and equating equal coefficients,

$$\lambda=a-\frac{\xi T}{1+KT}, \tag{6.2}$$

where $\lambda=\frac{u}{M_0}R^2T^2$, and $\xi=Rb_0$.

To solve for K, we define some quantity θ such that $\theta=\frac{1}{T}$

then $$\lambda=a-\frac{\xi}{\theta+K}, \tag{6.3}$$

and eliminating a $$\frac{\xi(\theta_2-\theta_1)}{(\theta_1+K)(\theta_2+K)}=\lambda_1-\lambda_2. \tag{6.4}$$

Similarly $$\frac{\xi(\theta_3-\theta_1)}{(\theta_1+K)(\theta_3+K)}=\lambda_1-\lambda_3, \tag{6.4.1}$$

and by division $$\frac{(\theta_1-\theta_2)(\theta_3+K)}{(\theta_1-\theta_3)(\theta_2+K)}=\frac{\lambda_1-\lambda_2}{\lambda_1-\lambda_3}, \tag{6.5}$$

and since λ may be evaluated for each experimental isothermal, K may be calculated directly.

The nature of the equation is such that K may be evaluated to one significant figure only, its value being 5×10^{-3}. Using this value for a calculation of b we have, $b=0.412$, from which the viscosity at 0° C. is 0.000131, compared with the measured value of 0.0001354, and using the value of K above, b at $-60°$ C. is 0.000116 against a measured value of 0.0001160 for carbon dioxide. Thus without the use of any results other than those used to determine the slopes of the isothermals, viscosities may be calculated over a long temperature range with an accuracy of about 2%. The nature of the viscosity temperature function has, however, to be assumed.

References

1. AMAGAT, E. H. Ann. chim. phys. 29: 68-136. 1893.
2. ANDREWS, T. Phil. Trans. 159: 575-590. 1869.
3. ANDREWS, T. Phil. Trans. 167: 421. 1877.
4. BRIDGEMAN, O. C. J. Am. Chem. Soc. 49: 1130-1138. 1927.
5. COOPER, D. LEB. and MAASS, O. Can. J. Research, 4: 283-298. 1931.
6. JEANS, J. H. The dynamical theory of gases, 4th ed. 1925.
7. JELLINEK, K. Lehr. d. phy. Chem. 1928.
8. LENNARD-JONES, J. E. Proc. Cambridge Phil. Soc. 22: 105. 1924.
9. MAASS, O. and MENNIE, J. H. Proc. Roy. Soc. A. 110: 198-232. 1926.
10. SUTHERLAND, B. P. and MAASS, O. Can. J. Research, 5: 428-443. 1932.
11. SUTHERLAND, W. Phil. Mag. 36: 507-531. 1893.
12. VAN DER WAALS. Die Kontinuitat des gasformigen und flussigen Zustandes. Leipzig. 1881.

THE CONDENSATION OF CERTAIN γ-KETONIC ESTERS WITH AROMATIC ALDEHYDES[1]

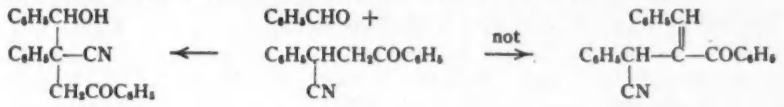
By C. F. H. Allen[2] and G. F. Frame[3]

Abstract

The condensation of methyl and ethyl α-phenyl-β-(para-substituted)benzoyl propionates with benzaldehyde and piperonal in the presence of sodium methylate, followed by acidification, has been found to produce cyclic compounds; the latter are shown to be lactols, six of which are described. The spontaneous ring closure is probably due to the highly branched chain. A mechanism for the reaction is proposed.

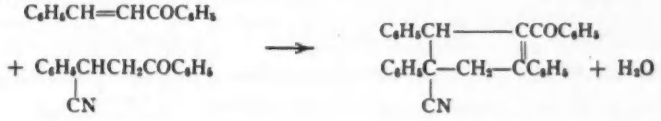
On oxidation with chromic acid, α-diketones are formed; the latter contain the aryl group introduced as aldehyde. The lactols resemble triphenylcarbinol in several respects, forming a chloride, methyl ether, and acetate on appropriate treatment, all of which, on hydrolysis, regenerate the lactol. They also give colored solutions with concentrated sulphuric acid, from which the starting material is recovered on addition to water. From this work it is evident that in arylated γ-ketonic esters the hydrogen atom alpha to the ketone carbonyl group is more active in alkaline aldol condensations than the hydrogen in the alpha position to the carbalkoxy carbonyl group; the observation of others, that the conjugated system $>C{=}C{-}C(=O){-}OR$ is more stable than $>C{=}C{-}C(=O){-}R$, has been confirmed.

In a previous investigation (12*) it was found that when benzaldehyde reacted with α-phenyl-β-benzoylpropionitrile (I) in an alkaline medium, the hydrogen in the position alpha to the cyano group was involved:



II I

In the preparation of α-phenyl-β-benzoylpropionitrile by treatment of benzalacetophenone with an aqueous solution of potassium cyanide, a high melting insoluble solid is the principal product unless the hydrogen ion concentration is carefully adjusted; this solid has been shown to be III, formed by addition of the nitrile first formed to a second molecule of unsaturated ketone, and loss of water (8).



III

[1] *Manuscript received May 20, 1932.*
Contribution from the Department of Chemistry, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.

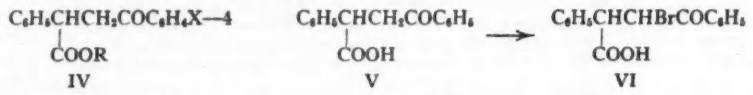
[2] *Assistant Professor of Chemistry, McGill University.*

[3] *Graduate student, McGill University, and holder, at the time, of a studentship and fellowship under the National Research Council of Canada.*

* *In the first sentence, 3rd line, page 1353, the word "nitrile" is ambiguous; it should read α-phenyl-β-benzoylpropionitrile.*

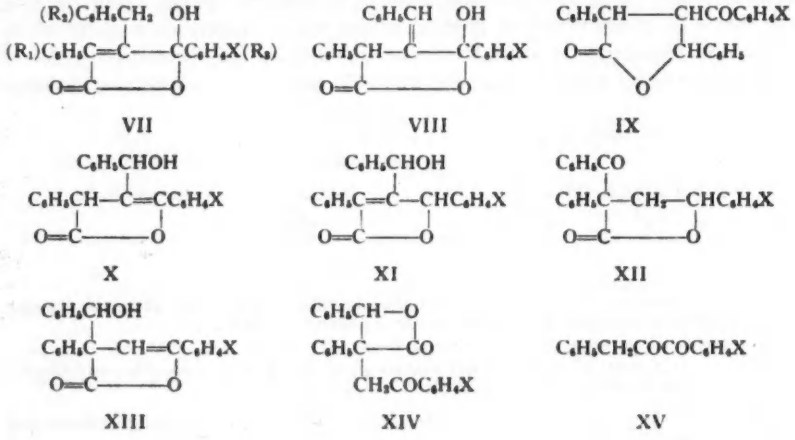
Thus the hydrogen atom alpha to the cyanogen radical is more active than the one alpha to the carbonyl group. Further examples are found in certain δ-ketonic nitriles (1, 12) that on bromination give almost entirely bromine substitution products of type A.

On account of these results it seemed desirable to investigate the ester (IV) corresponding to the nitrile (I) and determine which was the more active hydrogen. It was known that the acid (V) on bromination gave the mono-bromo-substitution product (VI), indicating that the hydrogen alpha to the ketonic carbonyl group was more reactive (14).



In this paper there will be described the products obtained from several esters (where X = Cl, Br, OCH_3) and benzaldehyde and piperonal. The aryl groups are "tagged" so that they can be followed through in reactions used to prove structure. Since a chlorinated lactone was first prepared this will be used in illustrating the reactions.

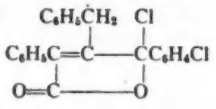
When methyl α-phenyl-β-(*p*-chloro-benzoyl) propionate and benzaldehyde are treated with sodium methylate in absolute methanol, a lactone, $C_{23}H_{17}O_3Cl$, is formed. As the same lactone results when the ethyl ester and ethyl alcohol are used, the carbalkoxy group must be involved in the formation of the lactone ring. It is possible to write eight possible isomeric structures, of which one (XIV) is a beta lactone; the latter is excluded because the product shows none of the characteristic properties of this type of cyclic compounds.



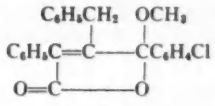
Any of the γ-lactones might equally well be formed; to distinguish between them has required a careful study of the reactions.

Potassium permanganate was rapidly reduced but the oxidation could not be controlled and a mixture of benzoic and *p*-chlorbenzoic acids was formed. Chromic acid was the most useful oxidizing agent. In this case benzyl *p*-chlorophenyl diketone (XV) resulted, which at once excluded substances having structures XII-XIV. By substituting piperonal for benzaldehyde and oxidizing the resulting lactone, piperonyl *p*-chlorophenyl diketone was obtained, showing that it was the aryl group introduced as aldehyde that appeared in the diketone. This would exclude a formula like VIII. Further, the substance was insensitive to ozone, whereas benzaldehyde would have been easily formed from VIII. Finally, the isomeric piperonal lactone (Formula VII, R_1 = 3,4-methylenedioxyphenyl, R_2 = phenyl, R_3 = *p*-chlorophenyl) has been made in this laboratory (21), and on oxidation found to form benzyl *p*-chlorophenyl diketone (XV). This evidence, taken altogether, excludes all the formulas except VII.

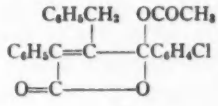
In the Grignard machine (15) the lactone shows one active hydrogen and two additions, indicating the presence of an hydroxyl group, but no esters were formed in the usual ways, as would be expected of substances X and XI; a lactone like IX would probably have no active hydrogen and should add three molecules of RMgX. On treatment of the lactone with acetyl chloride a chloride was obtained instead of an acetate, a characteristic property of tertiary alcohols. Thionyl chloride formed the same halide. This chloride (XVI) exhibited many of the characteristic properties of triphenylchlormethane. It formed a methyl ether (XVII) with absolute methanol, and an acetate (XVIII) with silver acetate. The lactone is thus a lactol.



XVI



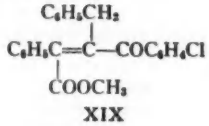
XVII



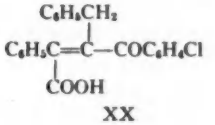
XVIII

On alkaline hydrolysis all of these gave a soluble alkali metal salt that on acidification regenerated the lactol.

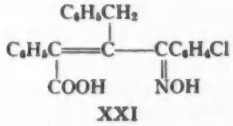
The latter is insoluble in water and aqueous sodium bicarbonate; it dissolves extremely slowly in hot sodium carbonate solution, probably because of the sodium hydroxide formed by hydrolysis of the latter. The soluble sodium salt is readily converted into a silver salt in the usual way, and the latter gives a methyl ester (XIX) when boiled with methyl iodide. The lactol is re-formed by alkaline hydrolysis of the ester and acidification. The only evidence for the presence of the tautomeric open chain form (XX) is the formation of an oxime (XXI).



XIX

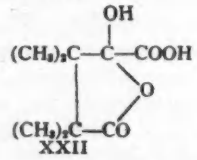


XX

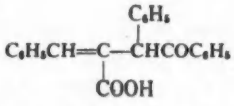


XXI

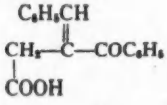
A detailed study of certain lactols has been made in connection with keto-lactol tautomerism (3, 6, 17, 22, 23, 24) as well as a few instances in suitably constituted substances having carboxyl and aldehyde groups in the required positions in the molecule (4, 9, 10; 19, 20). In nearly all the cases, typical reactions indicating both open chain and cyclic structure were observed, but with few exceptions, derivatives of the cyclic forms could only be obtained by drastic treatment (*e.g.*, with acetyl chloride or acetic anhydride). A stable lactol was formed only with substances having a very highly branched chain (XXII) (23).



XXII



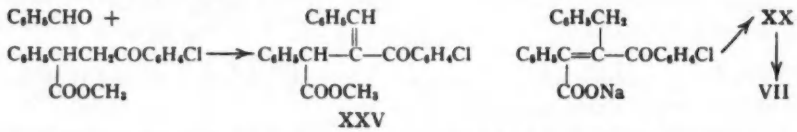
XXIII



XXIV

The most probable reason for the relative ease with which the lactols described in this paper are formed, simply acidification of the alkali salt, is doubtless the presence of the very highly branched chain, since very closely related substances (XXIII, XXIV) have stable open chain forms, and only give derivatives of a cyclic structure on treatment with acetic anhydride (5, 7).

The mechanism of the reaction forming the lactol is probably as follows: the ester first adds to the aldehyde in the ordinary way, followed by elimination of water. The point at which the H and double bond shift is uncertain but since Thiele (25) has shown that β, γ -esters of this type (XXV) isomerize in alkaline media to give α, β-esters the change is exactly what would be expected. The water eliminated in the first step in the alkaline solution hydrolyzes the ester to an alkali salt; on acidifying the solution the free acid at once cyclicizes to the lactol, the tendency to ring formation being greatly increased by the highly branched chain.

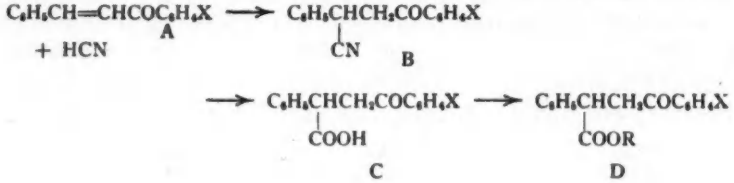


XXV

The condensation was not brought about by piperidine or diethylamine.

Experimental

A. Preparation of the esters. The esters were made as indicated by the outline:



(*1*) *The unsaturated ketones* (*A*). Benzalacetophenone was prepared according to the directions given in Organic Syntheses (13). Benzal *p*-chloro-, *p*-bromo-, and *p*-methoxyacetophenone were made by the following modification: to a mixture of 173 gm. of benzaldehyde, 183 gm. of *p*-chloroacetophenone, and 360 cc. of alcohol was added 78 cc. of 10% sodium hydroxide solution, and the whole cooled under the tap. The mixture became semi-solid in a few seconds. The whole was shaken frequently for 1.5 hr., then the solid filtered and purified. The yield was 267 gm. (93%) and the melting point 96° C. The *p*-bromo and *p*-methoxy homologues melted at 97° and 104° C. respectively.

(*2*) *The nitriles; addition of HCN* (*B*). α-Phenyl-β-benzoyl-propionitrile was prepared by the method given in Organic Syntheses (2). For the homologues it was found essential to operate for a longer time and at higher temperatures, and to use fresh alcohol in each run; *e.g.*, to 200 gm. of benzal-*p*-chloro-acetophenone, 2845 cc. of 95% ethyl alcohol and 87 gm. of glacial acetic acid was added 128 gm. of potassium cyanide in 354 cc. of water in 15 min., and the whole stirred at 35° C. for eight hours. After standing in the ice box, 193 gm. (87%) of α-phenyl-β-(*p*-chlorobenzoyl)propionitrile, m.p. 122° C., was obtained. The *p*-bromonitrile mixture was stirred for six hours and left in the ice box for two days. In preparing the *p*-methoxynitrile the temperature had to be kept at 50-55° C.; both were recrystallized from methyl alcohol.

TABLE I

YIELD, PROPERTIES AND ANALYSES OF THE NITRILES

Nitrile	Yield %	M.p. ° C.	Crystal form	Formula	Calcd. %	Found %
p-Bromo-	84	124	rectangular plates	$C_{16}H_{12}ONBr$	Br, 25.5	Br, 25.3
p-Methoxy-	65	62	long needles	$C_{17}H_{15}O_2N$	C, 77.0; H, 5.7	C, 76.8; H, 5.8

(*3*) *The esters* (*D*). Some of the esters were obtained by hydrolyzing the nitrile to the acid and esterifying the latter (18), and the others directly, by saturating absolute methyl alcoholic solutions of the nitriles with hydrogen chloride (16), using whichever was found to give the better yield (*e.g.*, with the *p*-chloro derivative, the first method gave a yield of 84% and the second 75%).

TABLE II

PROPERTIES AND ANALYSES OF THE ESTERS

Ester	M.p. ° C.	Crystal form	Formula	Calcd. %	Found %
Ethyl, *p*-chloro-	63	fine prisms	$C_{18}H_{17}O_3Cl$	Cl, 11.2	Cl, 11.5
Methyl, *p*-bromo-	129	rhombic plates	$C_{17}H_{15}O_3Br$	Br, 23.0	Br, 22.9
Methyl, *p*-methoxy-	97	dense prisms	$C_{18}H_{18}O_4$	C, 72.5; H, 6.0	C, 72.3; H, 5.9

The p-methoxyacid (C) though isolated (cf., first method) was not analyzed; by titration with standard alkali, a molecular weight of 275 was found (calcd. =284). It formed small scales from methyl alcohol.

B. Condensation of the esters with the aldehydes. A solution of sodium methylate prepared from 12.6 gm. of sodium and 212 cc. of absolute methyl alcohol was added to a mixture of 106 gm. of benzaldehyde, 212 cc. of absolute methyl alcohol, and 160 gm. of methyl α-phenyl-β-(*p*-chlorobenzoyl)propionitrile, and the whole refluxed for two hours. It was then acidified with acetic acid and the alcohol and unused aldehyde steam distilled. The residual organic product was taken up in ether, the latter dried with calcium chloride, and the solvent removed. The solid left was dissolved in the smallest possible amount of boiling methyl alcohol and deposited as fine prisms on cooling; the analytical sample was recrystallized from an ether-petroleum ether mixture. It is insoluble in petroleum ether, moderately soluble in alcohol and benzene, and very soluble in ether and acetone.

The same lactol resulted when ethyl alcohol and the ethyl ester were substituted in the above, and also when the reaction was carried out in alcohol that had been distilled from magnesium methylate. The homologues were prepared by essentially the same procedure, except that the ethereal extract was shaken with a saturated solution of sodium bisulphite when piperonal was used. Their properties are collected in Table III.

TABLE III
PROPERTIES OF THE LACTOLS

Lactol								Calcd., %			Found, %		
No.	R_1	R_2	R_3	Crystal form	M.p. °C.	Yield %	Formula	Hlg.	C	H	Hlg.	C	H
A	φ[c]	φ	4-Clφ	prisms[a]	134	77,82[c]	$C_{28}H_{17}O_4Cl$	9.4	73.4	4.5	9.3	73.5	4.5
B	φ	pip-[d]	4-Clφ	needles[b]	174	73	$C_{24}H_{17}O_3Cl$	8.4			8.3		
C	φ	φ	4 Brφ	prisms[a]	155	68	$C_{28}H_{17}O_3Br$	18.9			18.7		
D	φ	pip-	4-Brφ	needles[b]	171	88	$C_{24}H_{17}O_3Br$	17.2			17.6		
E	φ	φ	4-$CH_3O\varphi$	plates[a]	119	92	$C_{29}H_{20}O_4$		77.4	5.4		77.7	5.4
F	φ	pip-	4-$CH_3O\varphi$	needles[a]	162	92	$C_{25}H_{20}O_4$		72.1	4.8		72.2	4.7

[a] *From methyl alcohol;* [b] *from benzene;* [c] $\varphi = C_6H_5$; [d] *pip- = piperonyl;* [e] *from ethyl ester.*

C. General properties of the lactols (VII). The lactols are insoluble in sodium bicarbonate solution, but dissolve rapidly in cold, dilute sodium hydroxide, and are reprecipitated on acidification. They are recovered unchanged after solution in concentrated sulphuric acid. In the Grignard machine (15) they reacted with three moles of the reagent and evolved one mole of gas, indicating one active hydrogen and addition of two groups. They did not form esters (benzoates, *p*-nitro- and 3,5-dinitrobenzoates) nor a phenylurethane.

Oxidation. Potassium permanganate in acetone solution oxidized the lactols completely to the corresponding benzoic acids. Chromic acid in acetic acid did not react as rapidly; a 1,2-diketone was formed and separated from the unoxidized substance by crystallization. Some of the diketones were previously known. They were converted into quinoxalines by boiling with *o*-phenylenediamine in alcohol. The lactols (D, F) containing a piperonal

residue (R_2) on oxidation gave diketones that were so sensitive they could not be isolated. Even the *o*-phenylenediamine used in an attempt to get a quinoxaline was sufficiently alkaline to destroy them. In all instances, however, a deep violet-brown color was given with ferric chloride. A detailed description is given of the *p*-chlorlactol only.

In a small three-necked flask provided with a stirrer, thermometer, and dropping funnel, and surrounded by a cooling bath, were placed 20 gm. of the *p*-chlorlactol (VII A) and 150 cc. of glacial acetic acid, and a solution of 6 gm. of chromic acid in 15 cc. of acetic acid slowly admitted from the funnel, keeping the temperature below 30° C. After an hour the green solution was poured into water, extracted with ether and the extract well washed with water and dilute sodium carbonate solution. From the latter, on acidification, 3 gm. of a mixture of benzoic and *p*-chlorobenzoic acids were isolated, separated, and identified. The ethereal solution, on evaporation, left a residue of 10.6 gm.; it was taken up in methyl alcohol, filtered from a small amount of insoluble material* and recrystallized to a constant melting point of 103° C. A half-gram of the substance and an equal weight of *o*-phenylenediamine in 15 cc. of methyl alcohol was refluxed for five minutes, and precipitated by addition of water. On recrystallization, the quinoxaline melted at 132° C. These properties agree with those of benzyl *p*-chlorophenyl diketone (XV) as described by Jörlander (11). In a similar manner the other lactols were oxidized by chromic acid to yellow α-diketones. The properties are summarized in Table IV.

TABLE IV

PROPERTIES OF THE DIKETONES AND QUINOXALINES

Lactol used	Diketone					Quinoxaline			
	M.p. °C.	Form	Formula	Calcd. %	Found %	M.p. °C.	Formula	Calcd. %	Found %
A	103	plates	$C_{15}H_{11}O_2Cl$	C,69.6; H,4.2	C,69.5; H,4.2	132	Ref. 11		
B	161-5d.	needles	$C_{15}H_{11}O_4Cl$	Cl,11.7	Cl,11.6	161	$C_{22}H_{15}O_2N_2Cl$	Cl, 9.5	Cl, 9.8
C	122	plates	$C_{15}H_{11}O_2Br$			143	$C_{22}H_{15}N_2Br$	Br, 21.3	Br, 21.4
E	96	Ref. 11				138	Ref. 11		

Permanganate oxidation. Several oxidations were carried out, using 5 gm. of the lactol in 150 cc. of pure acetone, varying the amounts of permanganate and the temperature, but in every instance the result was a mixture of benzoic and *p*-chlorobenzoic acids (4.2 gm. in a typical case) which was separated into its components and identified by melting point and mixed melting points.

D. Properties of the chloride (XVI). The chloride was formed from the lactol and thionyl or acetyl chloride equally well. When 15 gm. of the *p*-chlorlactol was dissolved in an excess of the halide, warmed gently, and allowed to stand, 13.7 gm. of the solid chloride remained after the solvent was removed. After several recrystallizations from ether it formed glistening white needles,

**This solid, m.p. 202° C.; contained chlorine; only enough was obtained for one analysis. Found: C, 72.3; H, 4.2%—corresponding to $C_{28}H_{17}O_3Cl$. Since it was never isolated from other oxidations it was not further studied.*

m.p. 137° C. It is sparingly soluble in cold ether, insoluble in petroleum ether, and readily soluble in boiling ether, benzene, and acetone. Analysis: Calcd. for $C_{23}H_{16}O_2Cl_2$; Cl, 18.0%. Found: Cl, 17.8%. In a similar manner the *p*-bromlactol gave a chloride which crystallized in prisms, m.p. 132° C. Analysis: Calcd. for $C_{23}H_{16}O_2ClBr$: Cl, 8.1; Br, 18.2%. Found: Cl, 8.0; Br, 17.9%. It was impossible to get crystalline chlorides from the other lactols.

The acetate (*XVIII*). A mixture of 1.2 gm. of the *p*-chlor-chloride and 1 gm. of silver acetate in 15 cc. of absolute ether was refluxed an hour, filtered, and the ether allowed to evaporate. The residual solid was recrystallized from *n*-butyl alcohol; it formed shining, white, rectangular prisms, m.p. 157° C., insoluble in methyl and ethyl alcohols. Analysis: Calcd. for $C_{25}H_{19}O_4Cl$: Cl, 8.5%. Found: Cl, 8.6%. The same acetate was also formed by boiling for 3 min. 3 gm. of the lactol in 10 cc. of acetic anhydride containing a trace of sulphuric acid, pouring into ice water and extracting with ether; the yield was quantitative. A mixed melting point with the acetate above was not depressed.

Hydrolysis. A mixture of 0.5 gm. of the acetate, 50 cc. of methyl alcohol, and 9 cc. of concentrated ammonium hydroxide was left over night at 30° C. After neutralizing by addition of dilute acetic acid, crystals of the lactol separated. These showed no depression of the melting point when mixed with the lactol.

The methyl ether (*XVII*). A solution of 11 gm. of the chloride in 75 cc. of methyl alcohol was refluxed for two hours. On cooling, the methyl ether separated quantitatively, in dense white prisms, and was recrystallized from methyl alcohol, in which it is very soluble hot. Analysis: Calcd. for $C_{24}H_{19}O_3Cl$: CH_3O, 7.9%. Found: CH_3O, 7.6%.

Hydrolysis. On refluxing for 15 min. 1 gm. of the ether with 15 cc. of 10% methyl alcoholic potash and allowing to stand, the potassium salt of the acid (XX) separated, and was analyzed without attempting purification. Analysis: Calcd. for $C_{23}H_{16}O_3ClK$: K, 9.4%. Found: K, 8.8%. On adding acid to its aqueous solution, the lactol was precipitated and identified by a mixed melting point. The ether was not affected by ammonium hydroxide.

The methyl ether of the *p*-bromlactol was prepared in a similar manner from the corresponding chloride. It separated from methyl alcohol, in which it is only moderately soluble hot, as rectangular plates, m.p. 75° C. Analysis: Calcd. for $C_{24}H_{19}O_3Br$: CH_3O, 7.1%. Found: CH_3O, 7.2%. It was likewise hydrolyzed by alcoholic potash, the *p*-bromlactol precipitated by addition of acid, and its identity shown by a mixed melting point.

E. The methyl ester (*XIX*). The methyl ester could not be prepared by refluxing an alcoholic solution of the lactol and a trace of mineral acid (cf. Ref. 7) but was easily obtained through the silver salt.

Aqueous silver nitrate was added to 15 gm. of the lactol dissolved in an equivalent amount of sodium hydroxide solution, as long as a precipitate formed. The latter was filtered, and washed thoroughly with water, alcohol, and ether, and dried in a vacuum desiccator. Analysis: Calcd. for $C_{23}H_{16}O_3ClAg$:

Ag, 22.3; Cl, 7.4%. Found: Ag, 22.9; Cl, 7.6%. A suspension of 18.2 gm. of this silver salt in 75 cc. of absolute ether and 10 cc. of methyl iodide was refluxed 0.5 hr., filtered, and the solvent allowed to evaporate. There was left 7 gm. of ester, which after several recrystallizations from methyl alcohol formed short white needles, m.p. 87° C. It was only sparingly soluble in the cold alcohol but dissolved readily on being heated. Analysis: Calcd. for $C_{24}H_{19}O_3Cl$: Cl, 9.1%. Found: Cl, 9.1%.

Hydrolysis. Half a gram of the ester was refluxed with 10 cc. of 10% methyl alcoholic potash for 15 min., the solution neutralized with acetic acid and poured into water. The precipitated lactol was collected, recrystallized, and identified by a mixed melting point.

F. The oxime (XXI). The oxime of the *p*-chlorlactol (VII) was formed in the usual way in dilute alcoholic acetic acid, and purified by recrystallizing from dilute methyl alcohol. It formed short needles, m.p. 160° C., moderately soluble in cold alcohol and very soluble in hot alcohol and ether. Analysis: Calcd. for $C_{23}H_{18}O_3NCl$: N, 3.6%. Found: N, 3.5%.

References

1. Allen, C. F. H. J. Am. Chem. Soc. 47: 1733-41. 1925; 49: 1112-5. 1927.
2. Allen, C. F. H. and Kimball, R. H. Organic Syntheses. 10: 80-1. 1930.
3. Barat, C. J. Ind. Chem. Soc. 7: 321-39. 1930; 8: 699-710. 1931.
4. Blaise, E. E. and Courtot, A. Bull. soc. chim. 35: 989-1004. 1906.
5. Borsche, W. Ber. 47: 1108-21, 2708-2722. 1914.
6. Bredt, J. Ann. 256: 314-340. 1890.
7. Erlenmeyer, E. Jun. and Lux, M. Ber. 31: 2224-38. 1898.
8. Hann, A. C. O. and Lapworth, A. J. Chem. Soc. 85: 1356-70. 1904.
9. Hill, H. B. Am. Chem. J. 3: 33-51. 1881.
10. Hill, H. B. and Cornelison, R. W. Am. Chem. J. 16: 277-307. 1894.
11. Jörlander, H. Ber. 50: 406-21. 1917.
12. Kohler, E. P. and Allen, C. F. H. J. Am. Chem. Soc. 46: 1525-34. 1924.
13. Kohler, E. P. and Chadwell, H. M. Organic Syntheses. 2: 1-3. 1921.
14. Kohler, E. P. and Goodwin, R. C. J. Am. Chem. Soc. 49: 219-27. 1927.
15. Kohler, E. P. and Richtmyer, N. K. J. Am. Chem. Soc. 52: 3736-8. 1930.
16. Kohler, E. P. and Shohan, J. B. J. Am. Chem. Soc. 48: 2425-34. 1926.
17. Kon, G. A. R., Stevenson, A. and Thorpe, J. F. J. Chem. Soc. 121: 650-65. 1922.
18. Lapworth, A. and Wechsler, E. J. Chem. Soc. 97: 38-48. 1910.
19. Meerwein, H. et al. J. prakt. Chem. 116: 229-75. 1927.
20. Meyer, H. Monatsh. 25: 491-9. 1904.
21. Normington, J. B. McGill University. Private communication.
22. Qudrat-i-Khuda. J. Chem. Soc. 128: 201-9. 1929; 129: 206-13. 1930; J. Ind. Chem. Soc. 8: 215-22. 1931.
23. Rothstein, E. and Shoppee, C. W. J. Chem. Soc. 126: 531-4. 1927.
24. Rothstein, E., Stevenson, A. and Thorpe, J. F. J. Chem. Soc. 127: 1072-80. 1925.
25. Thiele, J. et al. Ann. 319: 155-225. 1901.

THE EFFECT OF AGING ON THE ACTIVITY OF BAKER'S YEAST[1]

By R. K. Larmour[2] and S. F. Brockington[3]

Abstract

Yeast stored in cakes on ice showed little evidence of change in activity, as expressed in loaf volume, during the first 19 days; thereafter the loaf volume increased until the yeast was 30 days old; after this it decreased but never became as low as with the fresh yeast. The rate of carbon dioxide production was quite constant up to 26 days; thereafter it increased somewhat and maintained a higher though more irregular rate until the end of the series when the yeast was 56 days old.

Introduction

Flour is such a complex system of compounds that the task of assessing its value and of making accurate comparisons is very difficult and subject to large experimental error. Even in the case of a test such as the viscosity test, in which the added ingredients are simple chemical compounds and in which no manual technique is involved, slight changes in the conditions produce so profound an effect that the error of replication is large. The baking test involves manual technique which introduces still greater errors due to the personal factor of the operator. This factor has been extensively investigated by Geddes, Goulden, Hadley and Bergsteinsson (3) and by Merritt and Blish (6).

If all the ingredients used in bread making were simple chemical compounds such as water, salt and sugar, the errors observed could be attributed to manipulation, but another biological substance, yeast, must be included. Thus, there are two uncontrolled factors, the personal factor and the yeast factor, and as no one has yet been able to control the former it is very nearly impossible to segregate the variability that should properly be allocated to the latter. Whether or not the variability of the yeast contributes significantly to the total error of the baking test is a question still to be answered. The investigations of Werner and Siedhoff (7), Cook and Malloch (2), and Jorgensen (5) show that yeasts of different brands may vary considerably. Herman and Hart (4), on the other hand, tested two different brands of baker's yeast and found no appreciable difference in the baking results. Thus, all that can be said of different brands is that they may vary.

The product sold under one brand may also vary. Cook and Malloch (2), using eight samples of one brand observed the very large range, 289-416 cc., in the amount of carbon dioxide evolved in one hour. Another brand showed a range of 193-224 cc. for five samples. It is evident that careful factory

[1] *Manuscript received May 2, 1932.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Canada, with financial assistance from the Saskatchewan Agricultural Research Foundation and the National Research Council of Canada.
Issued as Paper No. 33 of the Associate Committee on Grain Research, National Research Council of Canada.

[2] *Associate Professor of Chemistry, University of Saskatchewan.*
[3] *Graduate Assistant, Associate Committee on Grain Research, University of Saskatchewan.*

control may result in a large reduction of variability but, on account of its nature, yeast would be expected to exhibit a certain amount of variation, even under the most favorable conditions of production.

Another source of variability is found in the shipment of the product from the plant to the distributor, and thence to the baker. This is important in western Canada because much of the commercial yeast used is produced on the Pacific coast, or in eastern Canada, and in either case it is several days old by the time the user receives it. Although great care is used in packing yeast for shipment it seemed possible that, in a country where wide extremes of temperature are common, some variability in activity might arise from this cause. An observation made in this laboratory confirmed the belief that the age of the yeast has a profound influence on its activity. In the course of a study of variability of loaf volume there was used a cake of yeast that had been in storage on ice for eight weeks. The baking results obtained with this and with freshly delivered yeast by one baker using the same flour are shown in graphs A and B, Fig. 1.

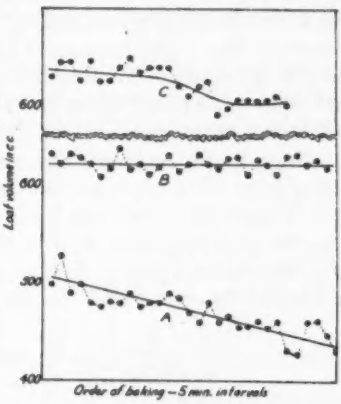


FIG. 1. *Three bakings made with one flour; A, with yeast eight weeks old; B, with yeast freshly delivered; C, with yeast three weeks old.*

The loaf volumes at the beginning of the series were lower than the values previously obtained with this flour and, as the baking progressed, there was a very marked decrease in volume until, at the end, the loaf volumes were approximately 75 cc. lower than at the beginning. This is not a usual occurrence although occasionally it has been suggested that there was a tendency for volume to fall off slightly toward the end of a run, as in graph C, Fig. 1. It was very important that definite information should be obtained on the behavior of yeast when kept in suspension at 30° C., because in our routine baking, yeast sufficient for 25 loaves is suspended at the beginning of the run and kept at 30° C. Furthermore, on the basis of the observation of Cook and Malloch (2) that yeast kept at 0° C. does not change appreciably in activity for periods up to 10 days, the authors had made a practice of having yeast delivered once a week and of storing it in contact with ice. It was necessary therefore to find out what changes might take place when yeast of varying age was kept suspended at 30° C.

Experimental

Series I

Twelve half-pound cakes of yeast were procured in one lot from the Winnipeg distributing plant and placed in cans on ice. Baking tests were made with a uniform sample of well aged, commercially milled, first patent flour, and all the bakings were performed by one operator. At each baking three doughs

were mixed at five-minute intervals with the freshly suspended yeast. The suspension was then stoppered and left on the panning bench until the end of the baking period, about 3½ hr., and shaken at intervals. At the end of this time three more doughs were mixed, using the old suspension. Averages of each set of three loaves are shown in Fig. 2. In this series of tests, 50 gm. of flour per loaf was used in place of 100 gm. During the first 11 days there was little change in the volume of loaves made with fresh suspension; with the exception of a slight decrease of about 8 cc. on the thirteenth day the volume was the same as on the first day, but thereafter a slight rise occurred and the loaf volume never fell below the 13-day value. The loaves made with the old suspension never equalled the others. The sharp drop in volume shown on the eleventh day seemed to be associated with high temperature of the yeast suspension. The container had been pushed back too close to the heaters and upon examination was found to be at a temperature of 42° C. The previous drop on the fourth and seventh days may have been due to the same cause. After the eleventh day the temperature of the suspension was checked frequently and kept very close to 30° C. After the twenty-first day, however, the loaves made with the old suspension dropped in volume and remained about 20 cc. lower than the check loaves. Disregarding the two drops previously mentioned, it appears that in the cases of both the fresh and old suspensions the activity tended to increase from the eleventh to the twentieth day, but the old suspension gave consistently lower values. After three weeks' storage on ice the yeast gave larger volumes than when it was fresh.

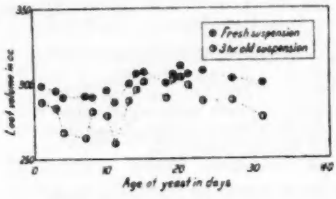


FIG. 2. *Effect of age of yeast on loaf volume, first series.*

Not satisfied with the results of this series of loaf volumes, mainly on account of the error due to failing to keep the suspended yeast at a fairly constant temperature, it was decided to repeat the experiment with greater care, and to make other tests of yeast activity.

TABLE I

EFFECT OF AGING OF YEAST ON LOAF VOLUME, STANDARD V FLOUR

Age of yeast, days	Loaf volume, cc.			Age of yeast, days	Loaf volume, cc.		
	Fresh suspension of yeast	Yeast suspension standing 3 hours at 30° C.	Mean		Fresh suspension of yeast	Yeast suspension standing 3 hours at 30° C.	Mean
7	650	635	642	29	687	673	680
12	653	632	642	33	683	710	697
14	653	640	646	41	670	657	664
19	652	675	664	49	670	658	664
26	663	660	662	56	685	688	686

Series II

For these experiments 12 half-pound cakes of yeast were procured in one lot. The number of replicate loaves was increased to five and the basic formula with 100 gm. of flour was used. Instead of storing the suspension on the bench it was kept in the proofing cabinet at 30 ± .5° C. during the interval between the first and second mixings. The average loaf volumes obtained are given in Table I and shown graphically in Fig. 3.

Usually the loaves made with the old suspension were smaller in loaf volume than those made with the fresh suspension, but there were two notable exceptions, namely, at 19 and at 33 days. On those dates the loaves made with the old suspension were unmistakably larger than those made with fresh suspension. In the last test, made with yeast 56 days old, there was no significant difference between the two sets of loaves. These data are inconclusive with respect to the effect of keeping yeast in suspension at 30° C. The average values were 667 and 663 cc. for the fresh and old suspensions respectively. It may be stated only tentatively that in most cases, the old suspension gave slightly lower loaf volume than the fresh suspension.

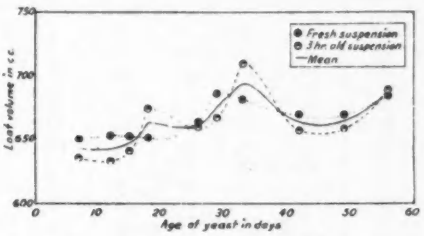


FIG. 3. *Effect of age of yeast on loaf volume, second series.*

In order to compare the trend of loaf volume with age of the yeast, the averages of all loaves baked in each test are shown as a curve in Fig. 3, each point representing the average volume of 10 loaves. It is unfortunate that there are not more data available for the period between 33 and 56 days, as the drop and final rise are rather peculiar and may be due partly to experimental error. Between 7 and 30 days the loaf volume increased with increasing age of the yeast. This improvement in volume was accompanied by improved bread characteristics. Interpreting the data broadly, it may be said that after the maximum at 30 to 33 days there was a gradual decrease in loaf volume, but it should be noted that in no case did the loaf volume drop below the volume observed at 7 days. The baking results with yeast varying in age from 7 to 15 days showed no significant variation and it is concluded, therefore, that for experimental baking yeast may be stored on ice for two weeks without undergoing any change detectable in the baking results.

Gas Production of Yeast of Various Ages

Concurrently with the baking tests, measurements were made of the gas produced in small doughs. These measurements were made by the method described by Bailey and Johnson (1), with certain minor modifications. The doughs were made up as follows: flour, 100 gm.; yeast, 3 gm; sugar, 2.5 gm.; salt, 1 gm.; water, 63 gm., and when taken from the mixer were quartered and placed in 150-cc. beakers. Two of these were placed in Mason jars containing

20% potassium hydroxide solution and two in jars containing 20% sodium chloride solution. As rapidly as possible the jars were immersed in a water bath at 30° C., and connected to the burettes. Readings were taken at 10-min.

TABLE II

EFFECT OF AGING YEAST ON GAS PRODUCTION IN DOUGH.
RATE OF GAS PRODUCTION IN CC. PER 10 MIN. INTERVAL

Time interval	Age of yeast in days										
	7	12	14	19	26	29	33	41	49	56	Average
	Cc. of CO_2 produced in 10-min. intervals.										
10	5	4	5	4	4	4	4	3	6	2	4.1
20	7	8	12	8	7	8	8	6	8	4	7.6
30	13	12	12	10	10	10	11	10	12	6	10.6
40	14	14	15	15	12	14	12	12	13	9	13.0
50	15	16	15	16	14	16	14	11	13	9	13.9
60	16	15	16	16	13	16	12	13	14	11	14.2
70	15	15	16	15	14	18	16	13	13	10	14.5
80	18	15	16	17	15	16	16	14	16	11	15.4
90	15	17	16	16	15	16	15	16	16	13	15.5
100	15	15	15	17	15	16	15	15	16	14	15.3
110	15	14	15	16	14	17	14	13	14	13	14.5
120	14	14	16	15	14	16	16	14	15	13	14.7
130	15	15	13	13	13	16	14	13	15	14	14.1
140	15	13	14	16	14	16	15	14	14	13	14.4
150	13	13	13	14	13	16	14	14	13	13	13.6
160	13	13	14	13	13	14	14	15	13	12	13.4
170	11	13	13	13	11	15	14	15	15	12	13.2
180	12	12	12	12	12	13	15	14	14	14	13.0
190	11	12	13	13	12	14	14	12	14	12	12.7
200	13	12	11	12	11	12	13	13	13	12	12.2
210	12	11	12	12	12	13	12	11	13	14	12.2
220	11	12	11	11	11	13	12	13	13	12	11.9
230	13	13	12	13	11	12	12	12	13	11	12.2
240	10	11	12	11	11	12	12	12	13	14	11.8
250	12	10	10	11	11	12	14	12	12	11	11.5
260	10	11	11	11	12	13	12	12	13	12	11.7
270	11	11	10	11	11	11	12	11	11	12	11.1
280	10	10	10	10	11	12	12	12	13	12	11.2
290	11	10	11	11	10	12	11	12	11	11	11.0
300	10	9	10	11	10	11	12	10	13	12	10.8
310	10	10	10	10	10	10	11	11	11	13	10.6
320	9	10	10	10	10	11	12	11	10	12	10.5
330	9	9	9	10	10	10	12	10	11	9	9.9
340	10	9	10	10	9	10	11	10	10	12	10.1
350	9	10	10	10	9	10	10	10	9		9.7
360	10	9	9	10	10	10	9	10	11		9.8
370	7	8	8	9	10	9	10	9	10		8.9
380	10	8	9	10	9	8	10	9	9		9.0
390	10	9	9	10	9	9	9	10	10		9.4
400	7	9	8	9	9	8	9	9	8		8.4
410	8	7	8	8	8	7	7	9	8		7.8
420	8	8	8	8	9	6	7		7		7.6
430	8	6	8	8	8	7	8				7.6
440	8	8	7		8	6	7				7.3
450	7	7	7		7	6	7				6.8
460	7	7	7		7		6				6.8
470	7	7	6								6.7
480	6	6	6								6.0
490	6	6									6.0

intervals. This was carried out with freshly suspended yeast and with yeast that had been kept in suspension for 3½ hr. at 30° C. As there was no significant difference in gas production of these two, only the data obtained with doughs made from the freshly prepared suspensions have been reported in Table II.

In dealing with data concerning the production of carbon dioxide, it is customary to make graphs of total carbon dioxide produced, volume attained and carbon dioxide lost, plotted against time. In this experiment all these data were collected but, as we were interested in comparing samples of yeast rather than different flours, it was considered that it would be better to calculate rates of gas production. Accordingly, in Table II the data are presented as the volume of carbon dioxide produced in each 10-min. period, and thus by inspection the variation in rate of gas production may be determined. To facilitate comparison of the rates of gas production by yeasts of various ages, the average rate per 20 min. has been plotted against time in Fig. 4. These curves, with the exception of that at 56 days, are very similar in shape and indicate that the rate of gas production in doughs was little affected by aging for a period of 49 days. In all cases the rate increased rapidly at first, attaining a maximum of 15-17 cc. per 10 min. at the end of 70-90 min. Thereafter, the rate of gassing decreased somewhat rapidly at first and then more slowly until at the end of three hours it had fallen to 10-11.5 cc. per 10 min. The curve for 56 days differed considerably from the others in that the initial increase in rate was slower and did not reach such a high maximum, but at the end of the third hour this yeast was producing carbon dioxide at a rate higher than shown by the 7-day-old yeast.

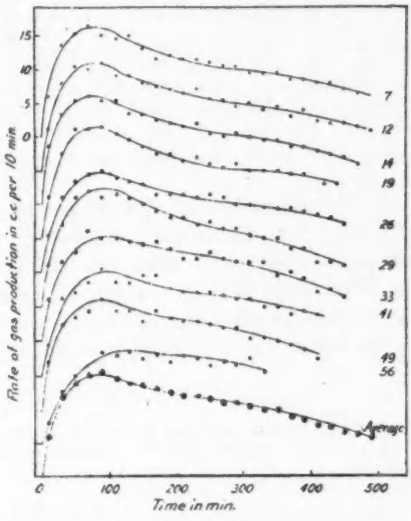


FIG. 4. *Rate of production of carbon dioxide by yeast of varying age.*

Probably the most crucial period in the dough is the proofing time, which in the authors' method is between 180 and 235 min. The rates of carbon dioxide production at the beginning and end of this period are shown in Table III. As the yeast became older there appeared to be an increase in rate of gas production during the period corresponding to the proof period. The average rate for the 60-min. interval, 180-240 min., was quite constant for the yeast samples ranging in age from 7 to 26 days; thereafter, in the 29-day-old sample there followed a rather abrupt increase. The last five samples, although showing considerable fluctuation in rate of carbon dioxide production during

this period on the whole produced gas at a greater rate than the first five of this series. The maximum rate for the series was obtained with the 49-day sample.

TABLE III

RATES OF CARBON DIOXIDE PRODUCTION AT THE TIMES CORRESPONDING TO THE BEGINNING AND END OF THE PROOFING PERIOD

Yeast sample, age in days	Rate of carbon dioxide production in cc. per 10 min. (from Table II)		Average	Yeast sample, age in days	Rate of carbon dioxide production in cc. per 10 min. (from Table II)		Average
	180 Min.	235 Min.			180 Min.	235 Min.	
7	11	10	11.7	29	14	12	12.6
12	12	11	11.6	33	14	12	12.7
14	13	12	11.6	41	12	12	12.1
19	13	11	11.9	49	14	13	13.0
26	12	11	11.3	56	12	14	12.3

The total amounts of carbon dioxide produced by these samples in periods of 3, 4 and 5 hr. are shown in Table IV. The values were fairly constant for all except the yeasts that were 29 and 56 days old, the former being higher and the latter lower than the others. The amount of carbon dioxide produced by the 49-day-old yeast was not significantly different from the amount produced by the yeast that was seven days old.

TABLE IV

TOTAL AMOUNT OF CARBON DIOXIDE PRODUCED BY THE VARIOUS YEAST SAMPLES IN PERIODS OF THREE, FOUR AND FIVE HOURS

Period of gas collection, hr.	Age of yeast, days									
	7	12	14	19	26	29	33	41	49	56
	Total amount of carbon dioxide produced, cc.									
3	241	238	248	246	223	257	239	226	240	191
4	311	309	319	318	291	333	314	299	309	266
5	375	370	381	383	356	404	387	368	382	336

There is little correspondence between the rate of gas production or total amount of carbon dioxide produced, and the loaf volume. The loaf volumes increased from 7 to 33 days and thereafter fell off. The rate of gas production was fairly constant up to 26 days and then increased and maintained a somewhat irregular higher level for the remainder of the samples. The total gas production was remarkably constant for all samples except those that were 26, 29 and 56 days old. The mean of the 26 and 29-day samples was in agreement with the others, but the 56-day sample was decidedly lower.

Conclusion

In conclusion it may be stated that, between 7 and 19 days, yeast stored on ice undergoes no change in rate or amount of carbon dioxide production, neither is there any significant difference in baking results. Thereafter, the loaf volume increases until the yeast reaches an age of 30 or 33 days, after which it decreases but the value never becomes as low as the value obtained with 7-day-old yeast.

The rate of carbon dioxide production in doughs is quite constant up to an age of 26 days but thereafter it increases somewhat and maintains a higher, though more irregular, level until an age of 56 days is attained by the yeast.

References

1. BAILEY, C. H. and JOHNSON, A. H. Cereal Chem. 1: 293-304. 1924.
2. COOK, W. H. and MALLOCH, J. G. Cereal Chem. 7: 133-142. 1930.
3. GEDDES, W. F., GOULDEN, C. H., HADLEY, S. T. and BERGSTEINSSON, H. N. Can. J. Research, 4: 421-482. 1931.
4. HERMAN, R. S. and HART, V. M. Cereal Chem. 4: 157-183. 1927.
5. JORGENSEN, H. Cereal Chem. 8: 361-374. 1931.
6. MERRITT, P. P. and BLISH, M. J. Cereal Chem. 8: 267-292. 1931.
7. WERNER, E. E. and SIEDHOFF, W. Cereal Chem. 6: 196-201. 1929.

STUDIES IN THE VARIABILITY OF TUBERCLE BACILLI

V. ACID AGGLUTINATION AND ELECTROPHORETIC POTENTIAL IN *MYCOB. LEPRAE*[1]

By G. B. Reed[2] and B. G. Gardiner[3]

Abstract

Previous work has indicated that various species of acid-fast bacteria including the tubercle bacilli may be separated into S and R types on the basis of colony structure and virulence; some results suggest that the two types differ in respect to the surface potential charge on the individual organisms. In this paper it is shown that S and R types of *Mycob. leprae* suspended in distilled water show a difference in electrophoretic potential of approximately five times the probable error of the determinations. Suspensions of S organisms are shown to have an isoelectric point of pH 1.2 compared with a pH of 2.2 in the case of a suspension of R organisms. Although acid agglutination of the S and R suspensions was found to occur at widely different pH levels, the agglutination occurred at approximately the same electrophoretic potential for both types, namely, at about 18.2 millivolts.

Introduction

In an early study of bacterial variation by DeKruif (1) two types of the bacillus of rabbit septicemia were differentiated by acid agglutination. Northrop (13) and Falk (3, 4, 5) recently reviewed the rather extensive literature, which has largely developed since that paper, dealing with variation from the point of view of acid agglutination, and particularly with the correlation between electrophoretic potential and virulence of strains within a species. It has generally been observed that cultures of a particular species showing the highest electrophoretic potential show also the greatest virulence. In some instances these two characteristics constitute the only observable differences, as in the case of the diphtheria bacillus, although this point has been questioned particularly by Jones (7). In other cases such as the *Pneumococcus* there appears to be a correlation between potential, serological types, and virulence for white mice. Where clear-cut S and R forms have been differentiated it has been observed in several instances that the S types, based on colony structure, show the higher virulence and the higher electrophoretic potential whereas the R forms are avirulent or of low virulence, and exhibit a lower potential.

Among the acid-fast species it was shown recently by Kahn and Schwarzkopf (8, 9), that S forms of tubercle bacilli show a higher electrophoretic potential than the R types. In two earlier papers in this series, Reed and Rice (14, 15), it was shown that the S and R forms from a considerable group of cultures of tubercle bacilli differ conspicuously in acid agglutination. These two results, apparently measurements of the same set of factors, suggested the desirability of a more detailed analysis in the hope of uncovering charac-

[1] *Manuscript received March 31, 1932.*
Contribution from the Department of Bacteriology, Queen's University, Kingston, with financial assistance from the National Research Council of Canada.

[2] *Professor of Bacteriology, Queen's University.*

[3] *Graduate student, Queen's University.*

teristics of variant types of acid-fast bacteria which would lend themselves to quantitative analysis. The results discussed in this paper are concerned entirely with S and R forms of *Mycob. leprae*.

It has just been shown (14) that *Mycob. leprae* as carried in stock cultures in various bacterial collections consists of S forms, R forms, or mixtures of the two, together with a variety of intermediate types. In fluid cultures the S forms were shown to be highly unstable and to dissociate readily to R. The R forms on the other hand proved relatively stable, yet R to S dissociation was demonstrated. In addition to the colony structure it was shown that the two types differed in habit of growth in fluid media, in oxidation-reduction potential changes during growth, and more particularly in complement fixation and agglutination reactions with specific S and R antisera. The S type was shown to contain a specific S antigenic substance, a species antigen, and an acid-fast group antigen, while the R form was shown to possess the two latter but to lack the specific S antigen.

Acid Agglutination

Well-established strains of S and R *Mycob. leprae* grown on either solid media such as glycerol-egg, or on fluid media such as Proskauer and Beck's fluid were removed with a minimum of media and ground in a mortar with distilled water to form an even suspension of the bacteria. This was readily accomplished by first grinding the semidry mass from the culture and then adding the water drop by drop until an even paste was produced. The S form always formed a stable suspension, while the R form required more grinding

TABLE I

ACID AGGLUTINATION OF SEVERAL S AND R CULTURES OF *Mycob. leprae* NO. 513. THE S AND R BRACKETED IN THE FIRST COLUMN REPRESENT CULTURES GROWN AND EXAMINED UNDER EXACTLY PARALLEL CONDITIONS. THE + SIGNS INDICATE THE DEGREE OF AGGLUTINATION

Organisms	pH of media											
	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	5.0	6.0	7.0
S 513	+ +	+	−	−	−	−	−	−	−	−	−	−	−
R 513	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	−	−	−	−	−
S 513	+ +	+ +	−	−	−	−	−	−	−	−	−	−	−
R 513	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	−	−	−	−	−
S 513	+ +	+	−	−	−	−	−	−	−	−	−	−	−
R 513	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	−	−	−	−	−
S 513	+ +	+ +	−	−	−	−	−	−	−	−	−	−	−
R 513	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+	−	−	−	−	−
S 513	+ +	+	−	−	−	−	−	−	−	−	−	−	−
R 513	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+	−	−	−	−
S 513	+ +	−	−	−	−	−	−	−	−	−	−	−	−
R 513	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+	−	−	−	−	−

and slower additions of water, but where these precautions were taken R suspensions could be made which remained stable for several hours. The suspensions were then washed three times by centrifuging and resuspending with grinding. Equal volumes of the suspensions and Clark's phosphate-phthalate buffer solutions ranging from pH 2.6 to 7.0 were mixed in small tubes. These were incubated for one hour in a water bath at 37° C. and the agglutination results read at once, and after 24 hr. at room temperature. The two readings were generally the same, the only difference being in the intensity of the agglutination.

Table I indicates the results obtained with several S and R cultures of *Mycob. leprae* No. 513. These were well-established types which had produced only S and R colonies, respectively, for several culture generations on solid media. The titration results are from cultures of ages varying from 10 to 30 days grown on gentian-violet glycerol-egg or in Proskauer and Beck's synthetic fluid. The bracketed pairs in the first column of the table represent S and R organisms cultured and examined under exactly parallel conditions. It will be observed that the pH at which agglutination occurred was uniform for each type.

Agglutination results with several well-established S and R types from other cultures of *Mycob. leprae* are shown in Table II.

TABLE II

ACID AGGLUTINATIONS OF S AND R TYPES OF *Mycob. leprae*. THE + SIGNS REPRESENT THE EXTENT OF THE AGGLUTINATION

Organisms	pH of buffer solutions									
	2.6	2.8	3.0	3.2	3.6	4.0	4.4	5.0	6.0	7.0
S type										
S 513	+ +	+ +	±	−	−	−	−	−	−	−
S 65	+ +	+ +	−	−	−	−	−	−	−	−
S 509	+ +	−	−	−	−	−	−	−	−	−
S 516	+ +	+	−	−	−	−	−	−	−	−
S 517	+ +	−	−	−	−	−	−	−	−	−
R type										
R 513	+ +	+ +	+ +	+ +	+ +	+ +	−	−	−	−
R 65	+ +	+ +	+ +	+ +	+ +	+ +	−	−	−	−
R 512	+ +	+ +	+ +	+ +	+ +	+	−	−	−	−
R 519	+ +	+ +	+ +	+ +	+ +	+ +	−	−	−	−
R 521	+ +	+ +	+ +	+ +	+ +	+ +	−	−	−	−

The values stated in Table II represent the average of several determinations, as do those in Table I. It is apparent that the S types from the several cultures are similar in this respect, and quite different from the R types which are similar to each other.

Measurements of Electrophoretic Velocity

Electrophoretic velocity determinations were made with the Northrop (13) type of apparatus. In the earlier experiments suspensions of organisms in distilled water were used. These were prepared as described in the preceding section. As it has generally been observed in such measurements that washing the organisms was essential, this procedure was followed in all the earlier experiments. It was found, however, that when the organisms were grown on solid media and carefully removed, washing did not influence the results. All readings were taken at the lower stationary level, as recommended by Falk (4), at a distance of $\frac{1}{2}D+\sqrt{3}$ from the lower inner surface of the cell. The cell was calibrated as described by Mudd (11).

Triplicate cultures of S and R forms of *Mycob. leprae* No. 513 were grown for six to seven days on glycerol-egg media, suspended in distilled water, washed, and the electrophoretic velocity determined. At least 10 organisms were timed in each preparation examined and from these readings the probable error was calculated. The results shown in Table III indicate an average velocity in microns per second per volt per centimetre of 4.36 for the S type and of 3.11 for the R type. The difference, 1.25, is approximately five times the probable error of the individual determinations.

TABLE III

ELECTROPHORETIC POTENTIALS OF SUSPENSIONS OF TYPICAL S AND R CULTURES OF *Mycob. leprae* NO. 513, SIX TO SEVEN DAYS OLD. THOSE BRACKETED WERE CULTURED AND EXAMINED UNDER PARALLEL CONDITIONS

Type of organism	Impressed voltage	Number of readings	Average time in seconds	Speed in μ/sec./volt/cm.
S	126	10	7.46 ± .24	4.15 ± .13
R	126	10	9.60 ± .42	3.22 ± .14
S	126	10	7.05 ± .41	4.39 ± .26
R	126	10	9.43 ± .64	3.28 ± .22
S	126	10	6.81 ± .56	4.54 ± .37
R	126	10	10.87 ± .75	2.84 ± .20
				Average S = 4.36 ± .25, Average R = 3.11 ± .19, Difference = 1.25.

A second group of cultures of both S and R types of varying ages were examined by the same procedure. The results tabulated in Table IV indicate that the electrophoretic potential increases gradually up to about three weeks, and later shows a decrease, especially in very old cultures. The average values, it will be observed, are much higher than those indicated in Table III for young cultures, however, approximately the same average difference between the S and R types is apparent.

Use of the Falk Cell

In an endeavor to simplify the procedure, the depression slide cell as used by Falk (4) was tried out. It proved to be less satisfactory than the Northrop-Kunitz type of apparatus especially on account of the polarization which caused water currents resulting in rapid changes in the readings. However, a number of sets of reasonably satisfactory readings are summarized in Table V. It will be observed that they are from 1 to 2 μ/sec./volt/cm. higher than those secured under comparable conditions with the Northrop-Kunitz apparatus, but the relative values are very similar and the conclusion the same; namely, that the S variant has a higher electrophoretic velocity and therefore a higher negative electrical charge than the R type.

TABLE IV

MEASUREMENT OF ELECTROPHORETIC VELOCITY OF S AND R TYPES OF *Mycob. leprae* FROM CULTURES OF VARIOUS AGES, WASHED AND SUSPENDED IN DISTILLED WATER

Age in days	S type		R type	
	Reading in seconds	Velocity in μ/sec./volt/cm.	Reading in seconds	Velocity in μ/sec./volt/cm.
6	7.11 ± .4	4.36 ± .25	9.97 ± .60	3.11 ± .19
8			8.75 ± .30	3.27 ± .11
11	5.6 ± .53	5.1 ± .48	8.00 ± .24	3.625 ± .11
14	4.9 ± .73	5.92 ± .88	7.75 ± .28	3.74 ± .13
15	5.37 ± .38	5.4 ± .38	8.3 ± .36	3.01 ± .13
24	4.4 ± .54	7.0 ± .86	5.1 ± .357	6.1 ± .42
28	5.6 ± .425	5.18 ± .375		
Average		5.52 ± .537		4.11 ± .18

TABLE V

A COMPARISON OF THE ELECTROPHORETIC VELOCITIES OF SUSPENSIONS OF FOUR TO SIX DAY CULTURES OF R AND S TYPES OF *Mycob. leprae* IN DISTILLED WATER, USING THE FALK CELL

Type of organism	Volts per cm.	Time for 420 μ in sec.	Velocity μ/sec.	Number of readings	Velocity in μ/sec./volt/cm.
S type					
S	24.3	3.2	131.2	10	5.4
S	24.3	3.2	131.2	10	5.4
S	24.3	3.2	131.2	10	5.4
S	24.3	3.3	128.1	10	5.3
Average S					5.38
R type					
R	24.3	3.9	107.7	10	4.4
R	24.3	4.1	102.4	10	4.2
R	24.3	4.0	105	10	4.3
R	24.3	4.3	97.6	10	4.0
Average R					4.22

TABLE VI

THE ELECTROPHORETIC VELOCITIES OF AN EIGHT-DAY R CULTURE OF *Mycob. leprae* WASHED AND SUSPENDED IN A SERIES OF BUFFER SOLUTIONS

	pH of buffer solutions									
	5.9	4.9	3.9	3.0	2.6	2.2	1.9	1.6	1.4	1.2
	Time in seconds									
	15	14.2	26.2	32			102.4	68.8	52	40.8
	14.	14	27	30.2			100.4	70.2	50.8	46.2
	13.2	13.8	23.4	31.8			104.2	66.0	48.2	44
	13.6	15.6	29.8	32	Almost	No	96.0	78	58	38
	13	15	29.6	32	no	motion	102.0	72.6	54	40.6
	13.6	16.2	26.4	29	motion				62.4	50
	16.4	15	30.8	31.8					56.2	48.2
	15.8	15	25.8	30.2					61.8	42.4
	14.6	16.2	30.4	32					52.6	40
	13.2	16.4	32.6	29					52.2	48.2
Mean	14.24±.74	15.14±.60	28.2±1.55	31.0±.81			101.0±1.87	71.1±2.72	63.3±2.76	43.9±2.6
μ/s/v/cm.	−2.01±.10	−1.9±.07	−1.01±.06	−0.29±.02			+.28±.005	+.4±.02	+.4±.03	+.65±.03

Determination of Isoelectric Points

Although the results indicated in the previous sections showed a definite difference between R and S types, it seemed from the work, particularly of McCutcheon, Mudd, Strumia and Lucké (10), that more striking results might be secured by a determination of isoelectric points. For this purpose a series of Clark's buffer solutions, ranging from pH 1.2 to pH 13 were prepared. Freshly washed bacterial suspension (2 cc.) was added to 20 cc. of the desired

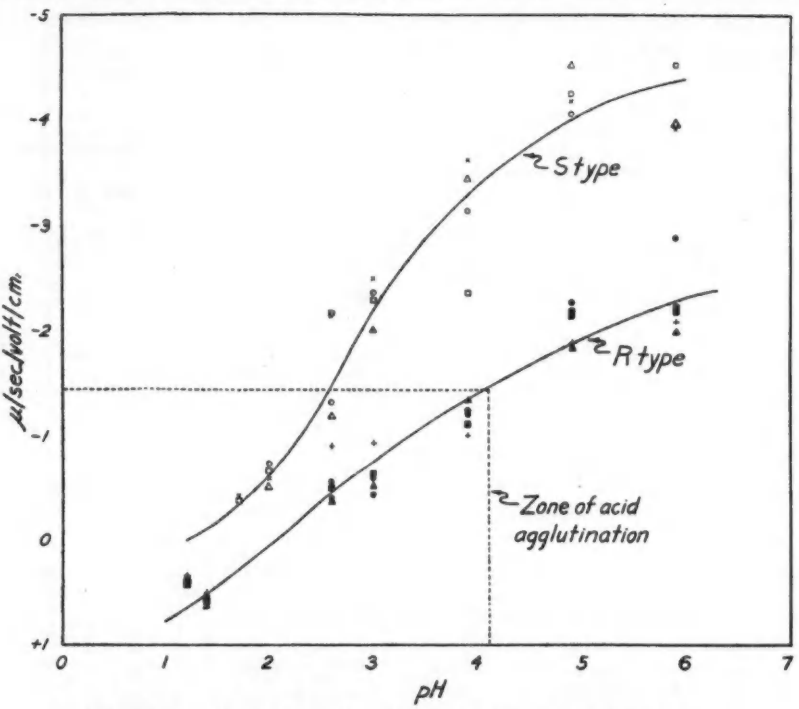


FIG. 1. *Curves of the electrophoretic potential of S (upper curve) and R (lower curve) Mycob. leprae suspended in buffer solutions of pH 1 to pH 7. The data are from Table VII :- S type;* × = 10 *day,* ○ = 14 *day,* □ = 15 *day,* △ = 28 *day cultures; R type;* + = 8 *day,* ● = 11 *day,* ▲ = 14 *day,* ■ = 20 *day,* ◑ = 41 *day cultures. The box enclosed by dash lines indicates the region of acid agglutination, data from Tables I and II.*

buffer mixture and electrophoretic readings were taken at once. More consistent results were obtained when the apparatus was flushed with a portion of the suspension in the buffer mixture just before readings were taken. It was soon found that there was no basic isoelectric point; attention was therefore focused on the acid end of the pH range. For this reason buffer solutions up to pH 7 only were used in most of the experiments.

Detailed results from the examination of an eight-day R type culture together with the calculated probable errors are shown in Table VI. It will

TABLE VII

RATE OF MIGRATION OF S AND R *Mycob. leprae* SUSPENDED IN BUFFER SOLUTIONS AT VARIOUS pH VALUES, ARRANGED TO SHOW THE ISOELECTRIC POINT. THE NUMBERS REPRESENT THE SPEED IN μ/SEC./VOLT/CM.

Age of culture in days	pH 5.9	pH 4.9	pH 3.9	pH 3	pH 2.6	pH 2.4	pH 2.0	pH 1.7	pH 1.5	pH 1.4	pH 1.2
S type											
10	3.92 ± .16	4.20 ± .24	3.64 ± .18	2.50 ± .12	2.15 ± .09		.60 ± .030	.42 ± .026	Very slow	Slower	No motion
14	3.97 ± .15	4.08 ± .18	3.15 ± .11	2.38 ± .09	1.32 ± .11		.73 ± .037		Very slow	Slower	No motion
15	4.53 ± .29	4.26 ± .18	2.38 ± .19	2.30 ± .11	2:16 ± .07		.67 ± .010	.40 ± .030	Very slow	Slower	No motion
28	3.97 ± .18	4.53 ± .14	3.45 ± .13	2.01 ± .06	1.20 ± .03		.51 ± .018		Very slow	Slower	No motion
Average	4.10 ± .195	4.27 ± .185	3.15 ± .15	2.30 ± .095	1.71 ± .075		.63 ± .024	.41 ± .028	Very slow	Slower	No motion
R type											
8	2.10 ± .10	1.90 ± .05	1.01 ± .055	.92 ± .021	.90 ± .037	Very slow	No motion	Very slow		+ .5 ± .025	+ .65 ± .038
11	2.90 ± .21	2.28 ± .21	1.21 ± .054	.60 ± .023	.57 ± .035	Very slow	No motion	Very slow		+ .47 ± .015	+ .64 ± .027
14	2.00 ± .07	1.86 ± .06	1.35 ± .104	.52 ± .036	.38 ± .015	Very slow	No motion	Very slow		+ .37 ± .011	+ .58 ± .025
20	2.20 ± .17	2.16 ± .08	1.12 ± .080	.64 ± .03	.50 ± .023	Very slow	No motion	Very slow		+ .42 ± .014	+ .61 ± .026
41	2.34 ± .14	2.2 ± .02	1.24 ± .090	.44 ± .01	.40 ± .017	Very slow	No motion	Very slow		+ .40 ± .009	+ .58 ± .030
Average	2.29 ± .14	2.08 ± .08	1.19 ± .077	.624 ± .024	.55 ± .025	Very slow	No motion	Very slow		+ .43 ± .015	+ .61 ± .029

be observed that the electrophoretic velocity varied from 2.01 μ/sec./volt/cm. at a pH of 5.9 to zero at about pH 2.2. Below pH 2.2 the sign of the charge was reversed, and motion toward the cathode became more rapid with increasing acidity. Results from the examination of a series of both S and R cultures of *Mycob. leprae*, in the manner indicated in Table VI, are summarized in Table VII, the same results being shown graphically in Fig. 1. The R types show very consistently an isoelectric region about pH 2.2; in more acid solutions the sign of the charge is reversed, becoming positive. The S organisms on the other hand exhibit an isoelectric point in the region of pH 1.2. These characteristics have shown a remarkable constancy in the many cultures examined.

In the case of mixtures of R and S organisms suspended in buffers of pH 1.5 to pH 1.7, organisms may be seen to move in both directions. At these acidities the S organisms retain a negative charge and move, though slowly, toward the anode, while the R organisms assume a positive charge, and move toward the cathode.

Comparison of Electrophoresis and Acid Agglutination

Ellis (2) found that the stability of an oil-water emulsion was very closely connected with the potential difference between the oil drops and the surrounding medium. Northrop (12), using *B. typhosus* found a similar condition, *i.e.*, that agglutination occurred whenever the potential difference fell below 15 mv. provided that the cohesive force was not affected.

It has been shown, Table I, that the R type of *Mycob. leprae* agglutinates with great constancy at pH 4.0 to pH 4.1, while the S type agglutinates at pH 2.6 to pH 2.8. In Fig. I, as already noted, the results of a series of potential determinations of S and R types have been plotted with the potential in microns per second per volt per centimetre as ordinates and the pH of the menstruum as abscissa. The pH at which acid agglutination occurs has also been indicated on both the S and the R potential curves. It will be observed that though the R agglutinate at pH 4 and the S at pH 2.6 to pH 2.8 these points are at approximately the same potential, 1.4 μ/sec./volt/cm. Or applying the Lamb-Helmholtz equation $P.D. = \frac{4\pi uv}{Kx}$ which, as adopted by Northrop becomes $P.D. = 13 \times \mu$/sec./volt/cm., these results then show a critical *P.D.* of 18.2 millivolts, which is in substantial agreement with Northrop's findings that typhoid bacilli agglutinate when the *P.D.* falls to 15 mv. or lower.

In other words, while the two types agglutinate in the same potential zone, it requires a much more strongly acid condition to bring the S type to this potential than in the case of the R type.

Summary

1. S and R types of *Mycob. leprae* have been shown to be distinguishable by acid agglutination. The S type agglutinates in buffer solutions of pH 2.6 to pH 2.8, the R type in solutions of pH 4.0.

2. Electrophoretic potential determinations have indicated a similar type difference. With the organisms suspended in distilled water the potential difference between the two types amounted to some five times the probable error of the determinations.

3. Isoelectric point determinations have provided more precise and consistent differences. The isoelectric point of the S types was found to be at pH 1.2 and that of the R at pH 2.2.

4. Although the acid agglutination of S and R types was found to occur at widely different pH levels it was also observed to occur at approximately the same electrophoretic potential for both types, namely, at about 18.2 millivolts.

References

1. DeKruif, P. H. J. Gen. Physiol. 4: 387-393. 1922.
2. Ellis, R. Z. physik. Chem. 78: 321-352. 1912.
3. Falk, I. S., Gussin, H. A. and Jacobson, M. A. J. Infectious Diseases, 37: 481-494. 1925.
4. Falk, I. S., Jacobson, M. A. and Gussin, H. A. J. Infectious Diseases, 37: 499-506. 1925.
5. Falk, I. S., Jensen, L. B. and Mills, J. N. J. Bact. 15: 421-450. 1928.
6. Jensen, L. B. and Falk, I. S. J. Bact. 15: 413-419. 1928.
7. Jones, L. Proc. Soc. Exptl. Biol. Med. 28: 883-884. 1931.
8. Kahn, M. C. and Schwarzkopf, H. Proc. Soc. Exptl. Biol. Med. 27: 381-383. 1930.
9. Kahn, M. C. and Schwarzkopf, H. Am. Rev. Tuberc. 23: 45-55. 1931.
10. McCutcheon, M., Mudd, S., Strumia, M. and Lucké, B. J. Gen. Physiol. 13: 669-681. 1930.
11. Mudd, S. and Mudd, E. B. H. J. Exptl. Med. 46: 173-195. 1927.
12. Northrop, J. H. J. Gen. Physiol. 4: 629-633. 1922.
13. Northrop, J. H. See Jordan, E. O. and Falk, I. S. The newer knowledge of bacteriology and immunology. Univ. of Chicago Press. 1928.
14. Reed, G. B. J. Bact. In press.
15. Reed, G. B. and Rice, C. E. Can. J. Research, 4: 389-398. 1931.
16. Reed, G. B. and Rice, C. E. Can. J. Research, 5: 111-121. 1931.

A MATHEMATICAL THEORY OF THE GROWTH OF POPULATIONS OF THE FLOUR BEETLE, *TRIBOLIUM CONFUSUM*, DUV.[1]

By John Stanley[2]

Abstract

Biological data relative to the growth of populations of the Confused Flour Beetle, *Tribolium confusum*, Duv. have been examined mathematically, the individual insects being treated as moving or stationary particles amenable to the formulations of the kinetic theory of gases.

Under certain simplified conditions, *i.e.*, prior to the time of the first hatching of eggs, it was found possible to integrate the differential equations, obtaining curves showing substantial agreement with the biological data.

Beyond this point, a function $\theta(t)$ enters, the form of which has not as yet been determined, though further work on this point will be carried out. Therefore, at present, only a cursory discussion of the use of the function, etc., is given.

Such information as can be gained regarding the population growth in the later stages, without knowledge of the actual form of $\theta(t)$, is also given.

Introduction

The object of this investigation was to work out, as far as possible, a mathematical theory to explain the growth of populations of the Confused Flour Beetle, *Tribolium confusum*, Duv., living in whole wheat flour, the cultures to be made up and handled as hereafter described. This theory is then applied as far as possible to actual experimental data, to show how the various environmental and biological factors operate to force the growths of the populations investigated along the paths which they are found to follow.

Owing to the fact that all the biotic constants necessary have not yet been evaluated, exact numerical solutions cannot be given. Furthermore, owing to the complexity of the differential equations, many of them cannot be integrated as yet. Hence, the application of the theory must for the present be confined to the use of such information as can be obtained from an explanation of the population trends.

In order to handle the great number of variables and parameters, a numerical subscript notation has been used, whereby it is possible to determine at once to which life-history stage, etc., a given symbol refers.

The Confused Flour Beetle, *Tribolium confusum*, Duv. occurs commonly as a pest of stored products, grain, flour, cereals, etc., in various parts of the world. In the United States of America, examinations of such infested materials from the more northern states show an infestation consisting largely of this species, while in the more southern states, the species, *T. ferrugineum*,

[1] *Manuscript received April 20, 1932.*

This paper was constructed from a thesis submitted to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, the work being done partly at the University of Minnesota, and partly at the Experiment Station of the Association of Hawaiian Pineapple Canners, Honolulu.

[2] *Junior Research Investigator, National Research Council, Ottawa, Canada; formerly Research Assistant, Department of Entomology, University of Minnesota, Minneapolis, and Department of Entomology, Experiment Station, Association of Hawaiian Pineapple Canners, Honolulu.*

Fab., is more likely to be found. The two species are almost identical in habits and form, and the theories set forth herein can be applied equally well to populations of *T. ferrugineum* Fab., with suitable changes in the values of the biotic constants.

General Statement of the Habits and Life History

The adults of *T. confusum*, Duv. are small brown beetles on an average 3.40 mm. long by 1.02 mm. wide, Table VII. The females, which form 50% of the adult population, lay small, white, ovoid eggs, at a rate which depends on the temperature, Table II. After a period of from 4 to 40 days, Table I,

TABLE I*

BIOTIC CONSTANTS OF *T. confusum* AT 75% RELATIVE HUMIDITY, AND AT THE TEMPERATURES INDICATED

Form	Expt.	Time in days	Mean time A and B	Standard deviation	Probable error	Coefficient of variability (mean)
32°C.						
Eggs	A†	4.42		0.136	0.092	
	B	4.42	4.42	0.137	0.093	3.093%
Larvae	A	17.38		0.773	0.521	
	B	17.30	17.34	0.744	0.501	4.372%
Pupae	A	5.32		0.716	0.482	
	B	5.44	5.38	0.694	0.467	13.105%
27°C.						
Eggs	A	6.05		0.130	0.088	
	B	6.03	6.04	0.105	0.071	1.950%
Larvae	A	22.33		0.634	0.427	
	B	22.51	22.42	0.511	0.345	2.557%
Pupae	A	8.72		0.871	0.588	
	B	8.57	8.69	0.738	0.497	9.305%
22°C.						
Eggs	A	14.10		0.261	0.176	
	B	14.08	14.09	0.237	0.160	1.760%
Larvae	A	60.49		4.851	3.273	
	B	61.73	61.11	4.875	3.289	7.959%
Pupae	A	16.94		0.885	0.597	
	B	18.78	17.86	2.078	1.402	8.645%
17°C.						
Eggs	A	38.80		0.980	0.661	2.000%
	B	38.83	38.82	0.897	0.534	2.418%

* *The author is indebted to Dr. R. N. Chapman for the data of Table I.*

† *These are not the A's and B's of Tables X to XIII.*

TABLE II*

EGG LAYING RATE OF *T. confusum* AT VARIOUS TEMPERATURES

Temp. °C.	Mean rate per ♀ day	Standard deviation	Probable error	Coefficient of variability
17	—	—	—	—
22	1.90	1.181	.797	62.234%
27	6.24	1.667	1.124	26.622%
32	10.73	2.887	1.948	26.912%

* *The writer is indebted to Dr. R. N. Chapman for the data of Table II.*

TABLE III

DIMENSIONS OF THE EGGS OF *T. confusum* *

Dimension	Min., mm.	Max., mm.	Mean, mm.	Stand. dev.
Data from Stanley (100 measured)				
Length	.52	.80	.64	.05
Width	.32	.50	.40	.02
Data from Brindley (3) (25 measured)				
Length	.62	.73	.64	.04
Width	.38	.47	.40	.02

* *With adherent flour.*

depending on the temperature, these eggs hatch to minute whitish larvae which wander in the flour and, during the course of their lives, moult their skins six times, increasing in size and vigor with each moult. At the last moult they change to the non-motile pupae. This series of changes takes from 17 to 61 days, again depending upon the temperature, as will be seen from Table I. The pupae remain motionless except for a slight wiggling movement for from 5 to 18 days, once more depending upon the temperature, Table I, and then, on the splitting of the skin, the new adult emerges. The new female adult does not lay eggs for a short time, the pre-oviposition period, which curiously enough is almost the same as the duration of the egg stage.

During life the adults and larvae of various ages wander about in an apparently aimless way in the flour, the adults, if female, laying eggs *en route*. Both adults and larvae are cannibalistic, living partly upon flour and partly upon such eggs, smaller larvae, and pupae as they can find and eat. There is no evidence, however, that they purposely search for this living food. They appear to be satisfied with that which is offered to them as a result of their movement through the flour. They require almost no care to rear, beyond seeing that the flour does not become filled with excreted waste.

TABLE IV

MISCELLANEOUS DATA FOR EGGS (STANLEY)

Weight of egg, 10,000 weighed (*en masse*), gm., 0.000,057,8 = W_3,(27°C).
Moisture in egg, mean of 3 samples of 10,000 each, 44.958%.
Available nutrient material in egg, gm. 0.000,025 = A_3
Percentage of eggs to hatch, 27°C. = 90, U_3 = .9

TABLE V

STADIA OF LARVAE OF *T. confusum* AT 27°C.

Stadium	First	Second	Third	Fourth	Fifth	Sixth
Length, days	2.43	3.63	3.03	3.27	3.39	6.67

NOTE:—*Values computed from Brindley's (3) data for 29.7°C.*

TABLE VI

WEIGHT OF ADULT BEETLES OF *T. confusum* FROM BRINDLEY (3), 80 OF EACH SEX WEIGHED

Sex	Min. wt., gm.	Max. wt., gm.	Mean wt., gm.	Stand. dev.
Male	.00140	.00155	.00148	.00006
Female	.00174	.00188	.00178	.00006

From the above general statement, it will be seen that *T. confusum* Duv. offers certain distinct advantages as a laboratory animal for population studies. It makes no webs or other structures in the flour, it is fairly resistant to handling, can be sifted from the flour to make population counts, and can live and develop over a wide range of temperature. For these reasons it has been used to some extent as an experimental animal, as the following survey of the literature will show.

TABLE VII

DIMENSIONS OF ADULT BEETLES OF *T. confusum* FROM BRINDLEY (3), 50 OF EACH SEX MEASURED

Dimension	Min., mm.	Max., mm.	Mean, mm.	Stand. dev.
Length	3.15	3.83	3.40	.14
Width	.85	1.11	1.02	.05

A Survey of the Literature

We shall confine ourselves in this survey to papers dealing with habits, life history, population growth, etc., as purely taxonomic papers are not of paramount importance with regard to the problem in hand.

The most important paper with regard to the insect is no doubt that of Chapman (7), in which he shows that the growth of a population of *T. confusum*, is dependent, at any one temperature, upon the size of the environment (a dish of flour), and upon the initial concentration of the beetles, but that the final concentration is independent of either the initial concentration or the size of the environment. Others have checked this work, (See Allee (1), Park (11)) and have obtained substantially the same results.

That there may be under certain conditions other limiting factors than eating is shown by the paper of Chapman (6), in which he speaks of a pungent gas given off by the beetle when irritated, and which causes the production of monstrosities if present in relatively small concentrations in the air around mature larvae. That this limiting factor is not considered in the following theory is due to the fact that monstrosities were seldom if ever observed, as the populations were always very carefully handled.

The life history has been worked out by Chapman (4) and by Brindley (3). The insect is also mentioned by Chapman (5).

Its nutritional requirements with regard to vitamins have been studied by Sweetman and Palmer (12).

Further studies have been made upon its life history by Holdaway (9), with regard to the production of intersexes, and finally there is the work of Gause (8)

in which he shows how changes in the various environmental factors may be correlated with the various equilibrium values assumed by the populations.

Four other papers worthy of mention, as they represent what is up to the present the best mathematical work on the subject of population growth, are those of Volterra (13, 14, 15), and Bailey (2).

The writer feels that some criticism may be levelled against Volterra's work on the grounds that so many assumptions have been made in order to simplify the mathematical treatment, that the entities considered can nowhere be found in the roster of living organisms.

Although the population counts on which Figs. 2 to 9, and the theory itself are based were made, not by the writer, but by Dr. R. N. Chapman, and his assistants, an explanation of the technique used would seem desirable.

Briefly then, whole-wheat flour was sifted through No. 8 silk bolting cloth to obtain an homogeneous fine flour containing sufficient vitamins for growth. This flour was then placed in the controlled temperature cabinets for a few days so that it might come into temperature and relative humidity equilibria with the air in the cabinets, and was then weighed out in lots having a weight of 32 gm. at 27° C., and 75% relative humidity (air). Previous to this, a number of adults were caged and the egg laying rate of each female carefully determined. Since violent shaking or sifting was found to alter the egg laying rate, these determinations were made by caging single females, and carefully rolling them out of the flour with a minimum of disturbance. The eight females for each duplicate lot were then selected to avoid the inclusion of any females having egg laying rates differing widely from the mean.

Eight males and eight of the selected females were then placed in each beaker with 32 gm. of flour and placed in the cabinets.

Counts were in general made every 10 days, the various life-history stages being separated by the use of bolting cloth sieves of various meshes. It was found that repeated counting at intervals of less than 10 days seriously altered the egg laying rate.

The flour was changed at each count, and on returning the beetles to the flour, great care was used to distribute them evenly through the mass.

Thus small controlled environments were set up in which the beetles lived and grew, and, provided care was taken to exclude certain parasitic mites and intestinal parasites, no trouble was experienced in obtaining parallel results with duplicate cultures. It was this close agreement between duplicate cultures that led to the following investigation subsequent to Dr. Chapman's pointing it out to the writer.

Part 1.

The Population Growth Under Conditions Such That Environmental and Biotic Resistance are Zero

It will be apparent that differential equations can be written, descriptive of the growth of the population, by the use of parameters descriptive of the insects and the environment.

In the following discussion the symbols pertaining to the various materials, flour and the different life-history stages, will be identified by the use of the following numerical subscripts, in accordance with the scheme outlined in the introduction.

Flour, 1; eggs, 2; first instar larvae, 3; second instar larvae, 4; third instar larvae, 5; fourth instar larvae, 6; fifth instar larvae, 7; sixth instar larvae, 8; pupae, 9; immature adults, *i.e.*, adults which have not passed the pre-oviposition period, 10; mature adults, 11.

Since however the point which we desire to make in Part I can be proved without a consideration of the various instars, etc., there is given below only a limited notation, sufficient for the matter in hand.

Let: N_0 = original number of adults.
N_2 = number of eggs at any time, T.
R = sex ratio, *i.e.* ratio of females to total.
ϵ = number of eggs laid per female per unit time.
T_0 = origin of time, *i.e.*, time at which population is set up.
$t_2(M)$ = time at which the laying of eggs of the M^{th} generation commences.
$t_3(M)$ = time at which the hatching of eggs of the M^{th} generation commences.
Γ_2 = number of days spent in the egg stage.
S = total time from egg to egg.

We shall now, under Part I, consider the idealized growth of a population, *i.e.*, on the supposition that there is no environmental resistance, no cannibalistic eating, and no variation in the values of the biotic or environmental parameters.

It will be seen, after careful consideration of the matter that, in any generation, there are two phases. For example, in the M^{th} generation there are the following:- (a) *Phase* M_1—from the commencement of laying by the M^{th} generation adults to the time of hatching of their eggs, *i.e.*, during the period of time, $t_2(M) < T < t_3(M)$. (b) *Phase* M_2—from the commencement of hatching of the M^{th} generation eggs to the commencement of laying of the $(M+1)^{th}$ generation eggs, that is during the period, $t_3(M) < T < t_2(M+1)$.

The equations descriptive of the growth of the egg population during the various phases are as follows.

Phase I_1

This phase covers the time interval, $t_2(1) < T < t_3(1)$, *i.e.*, from the commencement of laying of first-generation eggs, to the commencement of their hatching.

During this period,

$$N_2 = R\epsilon N_0 T$$

Where N_0 is the original number of adults, not necessarily 16, as in the experiments performed in connection with this particular problem.

Phase I_2

This phase covers the time interval $t_3(1) < T < t_2(2)$, *i.e.*, from the commencement of hatching of first-generation eggs to the commencement of laying of

second-generation eggs. During this phase, and during all subsequent time, the rate of increase of eggs is diminished by the hatching of first-generation eggs. The number of first-generation eggs which have hatched up to a time T is the number which were laid up to a time $(T-\Gamma_2)$, that is,

$$R\epsilon N_0(T-\Gamma_2).$$

Whence, during Phase 1_2

$$N_2 = R\epsilon N_0 T - R\epsilon N_0(T-\Gamma_2) = R\epsilon N_0\Gamma_2 = \text{constant}.$$

Phase 2_1

This phase covers the time interval, $t_2(2) < T < t_2(2)$, *i.e.*, from the commencement of laying of second-generation eggs to the commencement of their hatching. During this period, the rate of change of N_2 is increased by the production of second-generation eggs which are laid by adults formed from first-generation eggs laid during the period $T_0 < t < T-S$, where S is the time necessary for transformation of a newly laid egg to a fully mature adult. The group of N_0R first-generation eggs laid at $T = T_0 + \frac{1}{\epsilon}$ will mature and lay eggs in turn at $T = S + \frac{1}{\epsilon}$ and will lay $N_0R^2(T-S)\epsilon$ second-generation eggs up to a time T.

The next group, laid at $T = S + \frac{2}{\epsilon}$ will in turn produce second-generation eggs to the number of $N_0R^2[(T-S)\epsilon - 1]$ up to a time T. Thus the total number of second-generation eggs laid subsequent to a time, S, and up to a time T, will be, including the last group,

$$N = N_0R^2\left\{(T-S)\epsilon + [(T-S)\epsilon - 1] + [(T-S)\epsilon - 2] + \ldots [(T-S)\epsilon - (T-S)\epsilon]\right\}$$

$$= \sum_{\alpha_1=0}^{\alpha_1=(T-S)\epsilon} N_0R^2[(T-S)\epsilon - \alpha_1].$$

Whence, during Phase 2_1, the total number of eggs at any time T, during the period of the phase is,

$$N_2 = R\epsilon N_0\Gamma_2 + \sum_{\alpha_1=0}^{\alpha_1=(T-S)\epsilon} N_0R^2[(T-S)\epsilon - \alpha_1].$$

Phase 2_2

This phase covers the time interval, $t_2(2) < T < t_2(3)$, *i.e.*, from the commencement of hatching of second-generation eggs to the commencement of laying of third-generation eggs. During this phase and after, a negative term enters due to the hatching of the second-generation eggs. The number which hatch up to a time T is equal to the number laid up to a time $(T-\Gamma_2)$, that is,

$$\sum_{\alpha_1=0}^{\alpha_1=(T-S-\Gamma_2)\epsilon} N_0R^2[(T-S-\Gamma_2)\epsilon - \alpha_1].$$

Whence, at any time, T, during this phase,

$$N_2 = R\epsilon N_0\Gamma_2 + \sum_{\alpha_1=0}^{\alpha_1=(T-S)\epsilon} N_0R^2[(T-S)\epsilon - \alpha_1] - \sum_{\alpha_1=0}^{\alpha_1=(T-S-\Gamma_2)\epsilon} N_0R^2[(T-S-\Gamma_2)\epsilon - \alpha_1].$$

Phase 3_1

This phase covers the time interval $t_2(3) < T < t_3(3)$, *i.e.*, from the commencement of laying of third-generation eggs to the commencement of their hatching. In a manner analogous to that in which the second-generation eggs discussed under Phase 2_1 were formed, these third-generation eggs are formed from eggs laid during a time subsequent to $T = 2S$.

The second-generation eggs laid at a time $T = 2S + \frac{1}{\epsilon}$ are equal to N_0R^2, and, upon transformation to adults, will lay third-generation eggs to the number of $N_0R^3[(T-2S)\epsilon]$, up to a time T.

The second group of second-generation eggs laid in the interval $2S + \frac{1}{\epsilon} < T < 2S + \frac{2}{\epsilon}$ are, from the calculations of Phase 2_1, equal to $\sum_{i=1}^{i=2} R^3 i$ and lay third-generation eggs to the number of $\sum_{i=1}^{2} N_0R^3 i[(T-2S)\epsilon - 1]$ up to a time T.

Whence, by a continuation of the above reasoning, the total number of third-generation eggs laid up to a time T is,

$$N = \sum_{i=1}^{i=1} N_0R^3 i[(T-2S)\epsilon - 0] + \sum_{i=1}^{i=2} N_0R^3 i[(T-2S)\epsilon - 1] + \sum_{i=1}^{i=3} N_0R^3 i[(T-2S)\epsilon - 2] + \cdots\cdots\cdots + \cdots\cdots \sum_{i=1}^{i=(T-2S)\epsilon} N_0R^3 i[(T-2S)\epsilon - (T-2S-\frac{1}{\epsilon})\epsilon]$$

whence, $N = \sum_{\alpha_2=1}^{\alpha_2=(T-2S)\epsilon} \sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0R^3[(T-2S)\epsilon - \alpha_1]$.

Whence, during the interval, $t_2(3) < T < t_3(3)$

$$N_3 = R\epsilon N_0\Gamma_2 + \sum_{\alpha_1=0}^{\alpha_1=(T-S)\epsilon} N_0R^3[(T-S)\epsilon - \alpha_1] - \sum_{\alpha_1=0}^{\alpha_1=(T-S-\Gamma_2)\epsilon} N_0R^3[(T-S-\Gamma_2)\epsilon - \alpha_1] + \sum_{\alpha_2=1}^{\alpha_2=(T-2S)\epsilon} \sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0R^3[(T-2S)\epsilon - \alpha_1]$$

Phase 3_2

This phase covers the time interval, $t_3(3) < T < t_2(4)$, *i.e.*, from the commencement of hatching of third-generation eggs to the commencement of laying of fourth-generation eggs. By an extension of the reasoning employed under Phase 2_2, the additional negative term is

$$- \sum_{\alpha_2=1}^{\alpha_2=(T-S-\Gamma_2)\epsilon} \sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0R^3[(T-S-\Gamma_2)\epsilon - \alpha_1].$$

Phase 4_1

This phase covers the time interval, $t_2(4) < T < t_3(4)$ *i.e.*, from the commencement of hatching of fourth-generation eggs to the commencement of

laying of fifth generation eggs. By an extension of the reasoning used under Phase 3_1, the additional positive term is

$$\sum_{\alpha_3=1}^{\alpha_3=(T-3S)\epsilon} \sum_{\alpha_2=1}^{\alpha_2=\alpha_3} \sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0 R^4\left[(T-3S)\epsilon-\alpha_1\right].$$

Phase 4_2

This phase covers the time interval, $t_3(4)<T<t_2(5)$, *i.e.*, from the commencement of laying of fifth-generation eggs to the commencement of their hatching. Again a negative term enters, which can be shown to be

$$-\sum_{\alpha_3=1}^{\alpha_3=(T-S-\Gamma_2)\epsilon} \sum_{\alpha_2=1}^{\alpha_2=\alpha_3} \sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0 R^4\left[(T-3S-\Gamma_2)\epsilon-\alpha_1\right].$$

Whence, for phase M_1 where $t_2(M)<T<t_3(M)$

$$N_2=R\epsilon N_0\Gamma_2+\sum_{\alpha_1=0}^{\alpha_1=(T-S)\epsilon} N_0R^2\left[(T-S)\epsilon-\alpha_1\right]-\sum_{\alpha_1=0}^{(T-S-\Gamma_2)\epsilon} N_0R^2\left[(T-S-\Gamma_2)\epsilon-\alpha_1\right]$$

$$+\sum_{\alpha_2=1}^{\alpha_2=(T-2S)\epsilon}\sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0R^3\left[(T-2S)\epsilon-\alpha_1\right]-\sum_{\alpha_2=1}^{\alpha_2=(T-2S-\Gamma_2)\epsilon}\sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0R^3\left[(T-2S-\Gamma_2)\epsilon-\alpha_1\right]$$

$$+\ \ldots\ldots-\ldots\ldots+\ldots\ldots-\ldots\ldots+\ldots\ldots-\ldots\ldots+$$

$$+\sum_{\alpha_{(M-1)}=1}^{\alpha_{(M-1)}=[T-(M-1)S]\epsilon}\ \sum_{\alpha_{(M-2)}=1}^{\alpha_{(M-2)}=\alpha_{(M-1)}}\ \ldots\ldots\ldots\ \sum_{\alpha_{(M-i)}=1}^{\alpha_{(M-i)}=\alpha_{(M-i+1)}}\ \ldots\ldots\ldots$$

$$\ldots\ldots\ldots+\sum_{\alpha_2=1}^{\alpha_2=\alpha_3}\sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0R^{(M-1)}\left[\left\{T-(M-1)S\right\}\epsilon-\alpha_1\right].$$

During Phase M_2, where $t_3(M)<T<t_2(M+1)$ the additional negative term is

$$-\sum_{\alpha_{(M-1)}=1}^{\alpha_{(M-1)}=[T-(M-1)S-\Gamma_2]\epsilon}\ \sum_{\alpha_{(M-2)}=1}^{\alpha_{(M-2)}=\alpha_{(M-1)}}\ \ldots\ldots\ldots\ \sum_{\alpha_{(M-i)}=1}^{\alpha_{(M-i)}=\alpha_{(M-i+1)}}\ \ldots\ldots\ldots$$

$$\ldots\ldots\ldots\sum_{\alpha_2=1}^{\alpha_2=\alpha_3}\sum_{\alpha_1=0}^{\alpha_1=\alpha_2} N_0R^{(M-1)}\left[\left\{T-(M-1)S-\Gamma_2\right\}\epsilon-\alpha_1\right].$$

By an extension of the above method we may write equations descriptive of the growths of populations of any life-history stage.

The above equations demonstrate two important facts:

(a) That a population of this type, having distinct generations does not increase according to the compound interest law. It could probably be shown that such a law of increase does hold when T becomes very great, or if S is very small, as for instance in the case of bacteria and protozoa.

(b) That the population existing at any time is a function of its whole past history. Hence damage to a population is, theoretically at least, irreparable within finite time. In actual populations, owing to the action of environmental resistance, damaged populations do tend to return to the form which they would have had if undamaged, but never actually reach it.

Part 2

Population Growth Under Conditions Such That Environmental and Biotic Resistance are Greater Than Zero

The population growth will now be considered under the assumptions that temperature, relative humidity and the weight and chemical constitution of the flour are constant, while the various subtractive forces, resulting from natural mortality and from the eating of one form by another, are allowed full play.

These assumptions bring a very complicated system of forces into existence, hence the following general statement, supplementing that already given, may be of interest.

The original 16 adults, eight males and eight females, are placed in the flour and at once commence to lay eggs. At the same time, as a result of their movement through the flour, they again encounter some of their own eggs, and may eat them, certain conditions being satisfied. As a result of this eating and laying, the eggs tend to increase to the point where they are so numerous as to be found and eaten as rapidly as laid. Flour is of course eaten at the same time, a certain mathematical relationship existing between the amounts of egg material and flour consumed per adult per unit time.

Subsequent to hatching, the new larvae themselves prey upon the eggs, consume flour, and are in turn preyed upon by each other and by the adults. Young larvae also fall victims to older larvae.

At the time of the first pupation, the larval population is temporarily decreased by transformation to the pupal stage. At the same time, the egg population rises owing to the fact that egg-eating larvae are being transformed to non-egg-eating pupae. Thus at this point, except under certain special conditions to be discussed later (see page 666) the egg and pupal populations are increasing, and the larval population is decreasing.

Upon the commencement of emergence to the adult form, the passive pupae are changed over to voracious egg-eating adults, as yet too immature to lay eggs. Consequently, egg, larval, and pupal populations tend to decrease, while the adult population increases.

After a certain time, the pre-oviposition period, the oldest of the new adults *i.e*, the oldest female, begins to lay, and from this point on, the egg population increases to come into periodic fluctuating equilibrium with all the other forms. This increase in number of eggs is reflected in a later increase in larvae, and a still later and smaller increase in pupae. Occasionally there may be a later and small increase in adults. The eating of one form by another exerts a damping influence on the amplitude of these small increases. Figs. 4 to 9 will show the general truth of the above statements.

The problem of the numbers of contacts in unit time, occurring between insects moving in the flour

In order to discuss the manifold forces acting within the population, it is necessary to have some means of computing the rate at which contacts occur between the various individuals moving in the flour, since such contacts may result in the eating of some individuals by others.

If the individual insects be considered merely as moving particles, and owing to the almost infinitesimal degree of intelligence possessed, it is legitimate to make such an assumption, the problem may be handled by means of formulas from the kinetic theory of gases.

This theory (10) shows that three types of contacts may occur between particles moving in a given space: (a) contacts between a moving particle and a stationary particle, (b) contacts between two particles moving with the same speed, and (c) contacts between two moving particles having different speeds.

Thus, under case (a), where V is the volume of the space through which the particles are distributed, ν is the number of stationary particles, σ_1 their mean diameter, σ_2 the diameter of the moving particle, and μ its mean speed, the number of contacts in unit time between the moving particle and the ν stationary particles is,

$$N_a = \frac{\mu\pi\nu\left(\frac{\sigma_1+\sigma_2}{2}\right)^2}{V-\frac{2}{3}\pi\nu\left(\frac{\sigma_1+\sigma_2}{2}\right)^3}. \tag{1}$$

Under case (b) where both particles move with the same mean speed μ, and have the same diameter σ, and where the total number of particles per cubic unit is ν, the numbers of contacts per unit time between any one moving particle and the remaining $(\nu-1)$ particles is,

$$N_b = \frac{\frac{4}{3}\mu\pi(\nu-1)\sigma^2}{V-\frac{2}{3}(\nu-1)\sigma^3}. \tag{2}$$

Under case (c), where the two types of particles have mean speeds μ_1 and μ_2, mean diameters of σ_1 and σ_2, and where the number of one type is ν, the number of contacts in unit time between a single particle of the other type and the ν particles is,

$$N_c = \frac{\frac{1}{6\mu_1\mu_2}\left[-(\mu_1-\mu_2)^3+(\mu_1+\mu_2)^3\right]\pi\nu\left(\frac{\sigma_1+\sigma_2}{2}\right)^2}{V-\frac{2}{3}\pi\nu\left(\frac{\sigma_1+\sigma_2}{2}\right)^3}. \tag{3}$$

The value of $r = \frac{1}{6\mu_1\mu_2}\left[-(\mu_1-\mu_2)^3+(\mu_1+\mu_2)^3\right]$ depends on whether $\mu_1 > \mu_2$ or $\mu_2 > \mu_1$ for if $\mu_1 > \mu_2$ then,

$$r = \frac{3\mu_1^2+\mu_2^2}{3\mu_1},$$

and if $\mu_2 > \mu_1$ then,

$$r = \frac{3\mu_2^2+\mu_1}{3\mu_2^2}.$$

This difficulty may be overcome by writing

$$r = \frac{1}{6\mu_1\mu_2}\left[-(|\mu_1-\mu_2|)^3 + (\mu_1+\mu_2)^3\right] = F(\mu_1, \mu_2),$$

where the vertical lines around $\mu_1-\mu_2$ have their usual significance, meaning the *absolute value* of $\mu_1-\mu_2$.

In the case of contacts between individuals of the various life-history stages of *T. confusum*, it will be apparent that larva-egg, larva-pupa, adult-egg and adult-pupa contacts come under case (a); that larva-larva (where both larvae are of the same age) and adult-adult contacts come under case (b); and that larva-larva (where the two larvae are of different ages), and adult-larva contacts come under case (c).

Since, moreover, the volume $V-\frac{2}{3}\pi\nu\left(\frac{\sigma_1+\sigma_2}{2}\right)^3$ is merely the volume, G, of the flour, the above formulas reduce to

$$N_a = \frac{\mu\pi\left(\frac{\sigma_1+\sigma_2}{2}\right)^3}{G}, \tag{5}$$

$$N_b = \frac{\frac{4}{3}\mu\pi(\nu-1)\sigma^3}{G}, \tag{6}$$

$$N_c = \frac{F(\mu_1, \mu_2)\,\pi\nu\left(\frac{\sigma_1+\sigma_2}{2}\right)^3}{G}. \tag{7}$$

It is necessary at this point to discuss more fully the exact significance of σ_1 and σ_2 in the case of insects. It is not necessary that an insect come into actual physical contact with the main body wall of another insect to be aware of its presence. It may for example touch against a minute projecting bristle. As, then, a 'contact' will be defined as any approach of two entities of the population within such a distance of each other that mutual recognition of each other's presence occurs (or recognition by one party occurs, if the other be an egg or a pupa), it will be necessary to define what may be called "radii of perception".

It has been suggested to the writer that since the insects under discussion are assumed to have no intelligence, the term radius of *perception* is somewhat unfortunate. It is felt, however, that such is not the case, since by "intelligence" is meant, not the mere possession of powers of perception through the senses, but rather the possession of mental powers sufficient to make conscious and more or less elaborate decisions under definite conditions.

The radius of perception of a living entity for an infinitesimally small point is defined, then, as equal to the radius of a sphere whose volume V is

$$V = \int_{\alpha}^{\beta} \int_{Y_0}^{Y_1} \int_{Z_0}^{Z_1} J(X, Y, Z) dx\, dy\, dz, \tag{4}$$

where $J(X, Y, Z)$ is a surface surrounding the entity in space, beyond which its powers of perception are zero.

However, neither party in an insect contact such as have been discussed above has an infinitesimal diameter. Hence, where, for example, the radius of perception of an adult for an infinitesimal point is $\bar{r}_{11,\phi}$ and the radius of perception of a larva of some certain instar such that the correct subscript may in a general way be written as i, for the point is, $\bar{r}_{i,\phi}$, the radius of perception of either the larva for the adult, or *vice versa* is

$$r_{11,i} = r_{i,11} = \frac{\bar{r}_{11,\phi} + \bar{r}_{i,\phi}}{2} \text{ etc.}$$

In the case of contacts with eggs, the latter of course are incapable of perceiving anything so that, strictly, $r_{2,i} = 0$. It is obvious however that the quantity to be used in such a case in place of $\bar{r}_{2,\phi}$ is the mean radius of the egg.

Then where $M_{11.2}$, $M_{L.L}$ and $M_{11.L}$ are the numbers of contacts in unit time between adults and eggs, between generalized larvae of the same age, and between adults and generalized larvae respectively, and where μ_{11} and μ_L are the mean speeds of adults and generalized larvae,

$$\frac{dM_{11.2}}{dt} = \frac{N_{11} N_2 \mu_{11} \pi r_{11.2}^2}{G} \tag{8}$$

$$\frac{dM_{L.L}}{dt} = \frac{4 N_L (N_L - 1) \mu_{11} \pi r_{L.L}^2}{3G} \tag{9}$$

$$\frac{dM_{11.L}}{dt} = \frac{N_{11}\, N_L \cdot F(\mu_{11}, \mu_L) \pi r_{11.L}^2}{G} \tag{10}$$

Amounts of Flour Encountered by Adults or Larvae

Since adults and larvae eat flour, as well as eggs, other larvae and pupae, it is necessary to develop functions descriptive of the rate at which flour is encountered by moving adults or larvae. Theoretically this function could be developed in a manner similar to the above-mentioned formulas for contacts between adults and eggs, etc., but a much simpler and neater derivation can be given by reason of the more or less continuous nature of the flour medium.

It might be felt that inasmuch as an adult or larva is continually surrounded on all sides by flour, and as, by reason of its homogeneous nature, one portion of flour is indistinguishable from any other portion, the amount of flour brought to the attention of a moving insect in unit time should be independent of the mean speed of the insect. (It should be noted that in speaking of the senses of insects, no anthropomorphic concept is intended; the words are used simply because more suitable expressions are not available.)

The writer feels however that such is not the case, for he cannot help but think that (to use unfortunately an anthropomorphic analogy) a steady stream of material passing across the field of perception gives an impression of volume proportional to the distance travelled by the stream in unit time.

Consider an adult moving in a random way in a space, G, filled with flour. Clearly the adult does not bore out an exactly circular tunnel but, for ease of consideration, the tunnel will be considered as circular, and of such a radius ρ that $\pi\rho^2 = \int_C x dy$ where the expression on the right is the line integral taken in the positive direction around the boundary curve of a right section of the tunnel.

It is further assumed that the anterior surface of an adult cephalad of a certain plane of right section Q is defined by a function $\phi\ (x, y, z)$; that only the flour in a layer of thickness D over the surface $\phi\ (x, y, z)$ is perceptible to the adult as food, and that when, due to forward movement of the insect, a particle of flour passes to a position posterior to Q, it ceases to be perceptible as food. It is also assumed, for the moment, that flour is a perfect fluid, *i.e.*, frictionless and incompressible.

If now, the surface $\phi\ (x, y, z)$ be moved a distance dx along the longitudinal axis of the insect, a certain frustum of thickness dx will pass beyond Q and be lost to perception.

With the exception of infinitesimals of higher order, the volume of this frustum is:

$$dv = \pi(\rho+D+\rho)(\rho+D-\rho)dx$$
$$= \pi(2\rho D+D^2)dx.$$

Whence, on advancing the surface $\phi\ (x, y, z)$ at a rate μ_{11}, there passes across the field of perception of an adult, in unit time,

$$V = \int_0^{\mu_{11}} \pi(2\rho D+D^2)dx = \pi(2\rho D+D^2)\mu_{11},$$

which is the volume of a cylindrical shell of thickness D surrounding the bore of the tunnel cut out in the flour.

Then, where,

$M_{11.1}$ = volume of flour encountered by a mature adult up to a time T.

$M_{L.1}$ = a similar function for the generalized larva.

And where, for the sake of uniformity, we write:

$$r_{11.1}^2 = 2\rho_{11}D_{11}+D_{11}^2 \qquad r_{L.1}^2 = 2\rho_L D_L+D_L^2$$

Calling $r_{11.1}$ and $r_{L.1}$ the radii of perception for flour, we have:

$$\frac{dM_{11.1}}{dt} = \pi r_{11.1}^2 \mu_{11}, \quad \frac{dM_{L.1}}{dt} = \pi r_{L.1}^2 \mu_L.$$

In a practical case, however, flour is not in any sense a perfect fluid, but this makes no difference as far as the speeds μ_{11} and μ_L are concerned, as these are the speeds maintained in spite of the resistance of the flour. The fact of compressibility must however be taken into account, and this may be done by means of an arbitrary factor of compression, to be determined by experiment

for each type of flour and for each life-history stage. These factors are then of the form, K_3, K_4, K_5, K_6, K_7, K_8, K_{10}, K_{11}, according to the established notation for subscripts.

Including the above factors, where K_L is the subscript for the generalized larva,

$$\frac{dM_{11.1}}{dt} = K_{11}\pi r^2_{11.1}\mu_{11}, \qquad \frac{dM_{L.1}}{dt} = K_L\pi r^2_{L.1}\mu_L. \tag{12}$$

A Transformation of the Above Equations

So far the equations descriptive of rates of contact have been developed in terms of individual eggs, larvae, etc., but in order to determine the rates at which these various food materials are consumed it will be necessary to transform the above equations into others descriptive of the rates at which assimilable nutritive materials are encountered.

It would be difficult or even impossible to determine the exact requirements of each life-history stage in terms of the various fats, proteins, vitamins, etc., and if the various stages were at certain times dependent entirely upon one food and at other times entirely upon another, it would be necessary to have exact knowledge of the materials obtainable from each food source. However, as this is not the case, it is possible, without grave error, to make the assumption that each food material supplies all of the substances necessary to maintain the various entities feeding on it. It may be the case that eggs, for example, are lacking in some particular chemical substance if they are to function as the sole food, but this need not cause concern, as the necessary compound is obtainable from some source as evidenced by the vigorous growth of the feeders. That is to say, it does not appear that, throughout all the available foods, any compound is scarce to the point of detriment to the population.

Suppose that A_1, A_2, A_3 etc., are the assimilable percentages of nutrient material in the various life-history stages, W_2, W_3, etc., the weights of individuals of the various stages, and W_1 the density of uncompressed flour. We obtain, then, as equations descriptive of the rates at which assimilable nutrient materials are encountered, the following:

$$\frac{dY_{11.2}}{dt} = \frac{A_2W_2N_{11}N_2\mu_{11}\pi r^2_{11.2}}{G} \tag{13}$$

$$\frac{dY_{11.L}}{dt} = \frac{A_LW_LN_{11}N_L \cdot F(\mu_{11},\mu_L)\pi r^2_{11.L}}{G} \tag{14}$$

$$\frac{dY_{L.2}}{dt} = \frac{A_2W_2N_LN_2\mu_L\pi r^2_{L.2}}{G} \tag{15}$$

$$\frac{dY_{11.1}}{dt} = \frac{A_1W_1N_{11}K_{11}\mu_{11}\pi r^2_{11.1}G}{G} = A_1W_1N_{11}K_{11}\mu_{11}\pi r^2_{11.1} \tag{16}$$

$$\frac{dY_{L.1}}{dt} = \frac{A_1W_1N_LK_L\mu_L\pi r^2_{L.1}G}{G} = A_LW_LN_LK_L\mu_L\pi r^2_{L.1}. \tag{17}$$

It is now possible to set up the differential equations for the early stages of the population growth, except for one point discussed below.

It will be apparent that (considering the insect from a purely mechanistic viewpoint) there is a certain definite quantity of nutrient material which must be assimilated in unit time to carry on the processes of life during that unit time. (The question as to what would occur in vitamin-deficient foods need not enter here as the use of whole-wheat flour obviates the possibility of such deficiencies.)

In actual practice it is not certain that the various life-history stages feed each one at a constant rate throughout the day. However, as they were kept in darkness, and the flour environment is at all times invariant, and there is at all times an abundance of food, it is assumed, lacking evidence to the contrary, that assimilable materials are ingested at such an average and approximately constant rate that the maintainance ration of the same is obtained for each increment of time. It is apparent that such an assumption cannot exactly describe what goes on, as, if larvae of an age α happen to be singularly lacking in assimilable materials, an adult, while consuming one of them, cannot, perhaps, maintain this assumed rate of ingestion. However, this is not a grave matter, as the above assumption means that, with the exception of negligible quantities, the required amount of material is ingested over a finite time, even though the rate of ingestion may be small at some one instant.

This assumed, approximately constant rate of ingestion will be referred to as the "maintainance rate of ingestion", with the additional assumption that the digestive powers of all life-history stages are the same. Symbols of the form E_3, E_4, etc. will be used to denote it.

The Population During the Period $t_0 = t_2(1) < T < t_3(1)$

During this period, mature adults are laying eggs and at the same time are finding and eating them, whence the rate of change of the egg population is equal to the difference between the rates of egg production and egg consumption.

Let:

$C_{11.2}$ = number of individual eggs consumed by the N_{11} mature adults up to a time T.

$X_{11.2}$, $X_{11.1}$ = amounts of assimilable material, (by weight) obtained from eggs and flour respectively, and consumed by the N_{11} mature adults up to a time T.

$P_{11.2}$, $P_{11.1}$ = constant coefficients of preference of mature adults for eggs and flour respectively, as foods.

Then:
$$\frac{dN_2}{dt} = R\epsilon N_{11} - C'_{11.2} \tag{18}$$

From the definition of $P_{11.2}$ and $P_{11.1}$,
$$\frac{X'_{11.2}}{P_{11.2}\,Y'_{11.2}} = \frac{X'_{11.1}}{P_{11.1}\,Y'_{11.1}}. \tag{19}$$

From the definition of E_{11},

$$X'_{11.2}+X'_{11.1}=E_{11}N_{11}. \tag{20}$$

From (19)
$$X'_{11.1} = \frac{P_{11.1}Y'_{11.1}\cdot X'_{11.2}}{P_{11.2}Y'_{11.2}}. \tag{21}$$

Substituting in (20)

$$X'_{11.2} + \frac{P_{11.1}Y'_{11.1}\cdot X'_{11.2}}{P_{11.2}Y'_{11.2}} = E_{11}N_{11}, \tag{21}$$

$$X'_{11.2}=\frac{E_{11}N_{11}P_{11.2}Y'_{11.2}}{P_{11.2}Y'_{11.2}+P_{11.1}Y'_{11.1}}. \tag{22}$$

$$X'_{11.2}=\frac{\dfrac{E_{11}N_{11}P_{11.2}A_2W_2\mu_{11}\pi r^2_{11.2}N^2_{11}N_2}{G}}{\dfrac{P_{11.2}A_2W_2\mu_{11}\pi r^2_{11.2}N_{11}N_2}{G}+\dfrac{P_{11.1}A_1W_1K_{11}\mu_{11}\pi r^2_{11.1}GN_{11}}{G}}, \tag{23}$$

$$C'_{11.2}=\frac{X'_{11.2}}{A_2W_2}=\frac{E_{11}P_{11.2}r^2_{11.2}N_{11}N_2}{P_{11.2}A_2W_2r^2_{11.2}N_2+P_{11.1}A_1W_1K_{11}r^2_{11.1}G}, \tag{24}$$

$$C'_{11.2}=\frac{HN_2}{cN_2+d}, \tag{25}$$

Where $H=E_{11}\,P_{11.2}\,r^2_{11.2}\,N_{11}$; $c=P_{11.2}\,A_2\,W_2\,r^2_{11.2}$; $d=P_{11.1}\,A_1\,W_1\,K_{11}\,r^2_{11.1}\,G$.

Whence

$$\frac{dN_2}{dt}=\frac{R\epsilon N_{11}cN_2+R\epsilon N_{11}d-HN_2}{cN_2+d} \tag{26}$$

$$\frac{dN_2}{dt}=\frac{aN_2+b}{cN_2+d} \tag{27}$$

Where $a=R\epsilon N_{11}c-H$; $b=R\epsilon N_{11}d$.

Separating the variables and integrating:

$$\frac{cN_2}{a}+\frac{ad-bc}{a^2}\log(aN_2+b)=t+c_1 \tag{28}$$

When $t=0,\ N_2=0,$

So that
$$c_1=-\frac{ad-bc}{a^2}\log\ b,$$

Whence
$$T=\frac{c}{a}N_2+\frac{ad-bc}{a^2}\log\left(\frac{aN_2+b}{b}\right)=F(N_2). \tag{29}$$

Characteristics of the function $T=F(N_2)$, (See Fig. 1).

We may write,

$$aN_2+b=(R\epsilon N_{11}c+H)N_2+R\epsilon N_{11}d$$

$$aN_2+b=N_{11}P_{11.2}r^2_{11.2}[R\epsilon A_2W_2-E]N_2+R\epsilon N_{11}P_{11.1}A_1W_1K_{11}r^2_{11.1}G,$$

from which it is evident that a is less than zero in any real population, since $R\epsilon A_2 W_2$, the amount of assimilable nutrient material expended per female per day in the form of eggs, must be less than E_{11}, the total amount of assimilable nutrient material taken in per female per day, *i.e.*, $(R\epsilon A_2 W_2 - E_{11}) < 0$.

Hence, as b, c and d are easily seen to be greater than zero,

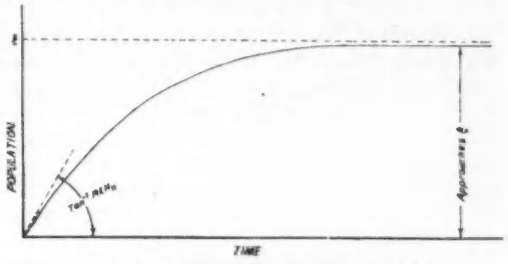


FIG. 1. *Graph of the function,* $T = F(N_2)$.

$$\frac{dN_2}{dt} \gtrless 0 \text{ as } N_2 \lessgtr -\frac{b}{a} = \xi . \tag{30}$$

It can further be shown that $T = F(N_2)$ may be written as a convergent alternating power series of the form,

$$N_2 = \alpha_1 T - \alpha_2 T^2 + \alpha_3 T^3 - \alpha_4 T^4 + \ldots\ldots , \tag{31}$$

and that $$\alpha_1 = R\epsilon N_{11} ,$$

whence $$\lim_{T \to 0} \frac{dN_2}{dt} = R\epsilon N_{11} .$$

Also, since $\frac{dN_2}{dt} = \frac{aN_2 + b}{cN_2 + d}$, $\lim_{N_2 \to 0} \frac{dN_2}{dt} = \frac{b}{d} = R\epsilon N_{11} = \lim_{T \to 0} \frac{dN_2}{dt}$.

It is also evident from an examination of (31) that $\lim_{T \to 0} N_2 = 0$ and it can further be shown by direct differentiation that $\lim_{N_2 \to \xi} \frac{d^2 N_2}{dT^2} = 0$

It is thus apparent that the egg population is equal to zero when T is equal to zero, and increases thereafter to approach a value ξ which it reaches only after an infinite time. (In an actual case, owing to the fact that the function $T = F(N_2)$ can exist only for integral values of N_2, this limit, ξ, may be reached in finite time, the population oscillating around the value ξ, and between the limits of the least integer greater than ξ, and the greatest integer less than ξ.)

Furthermore, when $T = T_0$, the egg population is increasing exactly at the rate at which the N_{11} mature adults lay eggs, namely, at the rate $R\epsilon N_{11}$. This rate decreases thereafter, reaching zero when N_2 equals ξ.

It is interesting to note the meaning of ξ. It represents the point at which the eggs are found and eaten as rapidly as laid. Thus, if eggs are introduced into the system by artificial means, as by adding them to the flour by hand, and stirring them in, they will be found and eaten more rapidly than the N_{11}

adults can lay, so that $\frac{dN_2}{dT} < 0$ and the egg population decreases to approach the limit ξ from above. Such conditions as have been described above occur only, of course, in the absence of hatching.

It is also of interest to examine the relationship between ξ and G, the size of the flour mass. Since hatching does not occur, N_{11} is a constant.

We may write, $b = R\epsilon N_{11} d = R\epsilon N_{11} P_{11.1} A_1 W_1 K_{11} r^2_{11.1} G = \gamma G$,

whence
$$\xi = \frac{\gamma G}{a},$$

and
$$\frac{d\xi}{dG} = \frac{\gamma}{a} = \text{a constant}. \tag{32}$$

Whence, the final egg population (in the absence of hatching), is proportional to the size of the environment. Since we may further write, $a = \theta N_{11}$,

where
$$\theta = P_{11.2} A_2 W_2 r^2_{11.2} (R\epsilon A_2 W_2 - E_{11})$$

and
$$b = \phi N_{11},$$

where
$$\phi = R\epsilon A_1 W_1 K_{11} r^2_{11.1} G$$

Then
$$\xi = \frac{\phi N_{11}}{\theta N_{11}} = \frac{\phi}{\theta}. \tag{33}$$

which is independent of the value of N_{11}.

Chapman (7) has shown that the limiting population reached with *T. confusum* is, by actual experiment, proportional to the size of the environment, and independent of the initial number of adults. It is true that at any temperature above 17°C. hatching occurs, so that the final population is a mixture

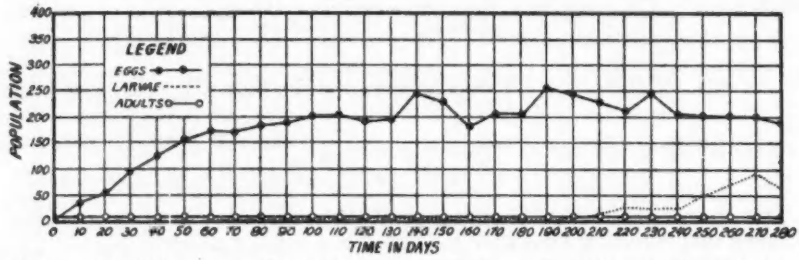


FIG. 2. *Population growth of T. confusum, Duv. at 17°C., mean of (A) and (B) populations.*

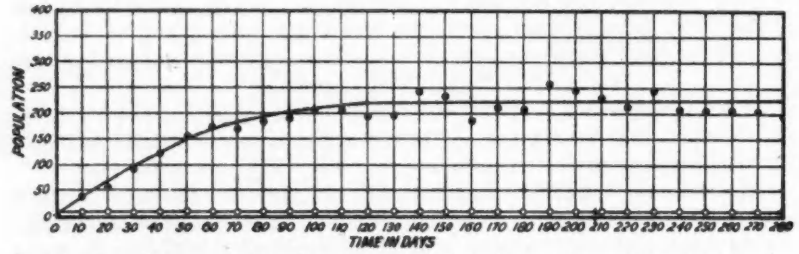


FIG. 3. *Smoothed curve for population growth of T. confusum, Duv. at 17°C., (See Fig. 1).*

of all stages, but it can at least be said that theory and experiment are in substantial agreement up to 17°C. Further elaboration of the theory will, it is believed, show similar agreement at higher temperatures.

At 17°C. the rate of hatching is so low that it can be neglected, and, as Figs. 2 and 3 show, the population curve follows very closely the theoretical curve of Fig. 1. It should be noted that the theoretical curve of Fig. 3 was not drawn from values computed from Equation (29), as, owing to lack of knowledge of several biotic constants, it is impossible to obtain such numerical solutions. It was however drawn on a basis of the information obtained as to its shape, from Equation (29). The claim to agreement is thus on the form of the curve only.

The Population Growth Subsequent to $T=t_3(1)$

Subsequent to $T=t_3(1)$, *i.e.*, after the first hatching of eggs commences, the problem assumes much greater complexity, due not only to the presence of larvae which act as predators, but also owing to the complicated functions descriptive of the rates of transformation of each life-history stage into the succeeding one.

The general form of the equations

By an extension of the reasoning used to determine Equation 18, it will be seen that the rate of change of the egg population is equal to the basic rate of laying of eggs, namely, $R\epsilon N_{11}$, minus the rate at which eggs as individuals are being eaten by the adults $(C'_{10.2}+C'_{11.2})$, minus the rate at which eggs are being eaten by the various larvae of different instars $(C'_{3.2}, C'_{4.2}, \ldots C'_{8.2})$, minus the rate at which eggs are arriving at hatching age (Z_3). It should be noted that not all eggs which arrive at hatching age actually hatch. A certain percentage shrivel up and die at this time. This matter will be referred to later.

Thus, in a purely general way, where all six larval instars are present

$$\frac{dN_2}{dt} = R\epsilon N_{11} - \sum_{i=3}^{i=8} C'_{i\cdot 2} - C'_{10.2} - C'_{11.2} - Z_3 \tag{34}$$

Certain assumptions are necessary in order that the differential equations descriptive of the growths of larval populations may be written. Some changes do occur in the biotic characteristics of a larva of any given instar during the time that it spends in that instar but, as these changes are relatively small, it will be assumed that the various parameters descriptive of each instar are constant throughout the life of that instar, and that the change from instar to instar is abrupt and discontinuous.

It has been stated that not all eggs arriving at hatching age actually hatch. The same thing applies to all subsequent transformations. Hence if U_3, $U_4 \ldots$ U_{11} be the percentages of deaths at egg-first instar, first instar-second instar, etc., transformations, then, when a form $(i-1)$ is arriving at the age of transformation to a form i at a rate Z_i, the form i is coming into existence at a rate U_iZ_i.

Then if N_j be the number of larvae of the form having subscript j at any time T, and $C'_{i,j}$ be the rate at which they are being consumed by other larvae of forms having the general subscript i, etc., then, in a purely general way,

$$\frac{dN_j}{dt} = U_j Z_j - \sum_{i=3}^{i=8} C'_{i,j} - C'_{10,j} - C'_{11,j} - Z_{j+1}. \tag{35}$$

It will be seen later that some or all of the C's may be zero, depending upon the circumstances at a particular time.

It is apparent that an equation similar to that descriptive of the growth of the egg population can be written in the case of the growth of the pupal population.

Evaluation of the C's

It is assumed, as again is practically true, except in the case of some of the smaller larvae, that no larva of a given instar can consume one of the succeeding instar, and that adults are immune from attack by any form, even by other

TABLE VIII

$\frac{X'_{11.1}}{Q_{11.1}}$	$\frac{X'_{11.2}}{Q_{11.2}}$	$\frac{X'_{11.3}}{Q_{11.3}}$	$\frac{X'_{11.4}}{Q_{11.4}}$	$\frac{X'_{11.5}}{Q_{11.5}}$	$\frac{X'_{11.6}}{Q_{11.6}}$	$\frac{X'_{11.7}}{Q_{11.7}}$	$\frac{X'_{11.8}}{Q_{11.8}}$	$\frac{X'_{11.9}}{Q_{11.9}}$	1	1
$\frac{X'_{10.1}}{Q_{10.1}}$	$\frac{X'_{10.2}}{Q_{10.2}}$	$\frac{X'_{10.3}}{Q_{10.3}}$	$\frac{X'_{10.4}}{Q_{10.4}}$	$\frac{X'_{10.5}}{Q_{10.5}}$	$\frac{X'_{10.6}}{Q_{10.6}}$	$\frac{X'_{10.7}}{Q_{10.7}}$	$\frac{X'_{10.8}}{Q_{10.8}}$	$\frac{X'_{10.9}}{Q_{10.9}}$	1	1
1	1	1	1	1	1	1	1	1	1	1
$\frac{X'_{8.1}}{Q_{8.1}}$	$\frac{X'_{8.2}}{Q_{8.2}}$	$\frac{X'_{8.3}}{Q_{8.3}}$	$\frac{X'_{8.4}}{Q_{8.4}}$	$\frac{X'_{8.5}}{Q_{8.5}}$	$\frac{X'_{8.6}}{Q_{8.6}}$	$\frac{X'_{8.7}}{Q_{8.7}}$	$\frac{X'_{8.8}}{Q_{8.8}}$	$\frac{X'_{8.9}}{Q_{8.9}}$	1	1
$\frac{X'_{7.1}}{Q_{7.1}}$	$\frac{X'_{7.2}}{Q_{7.2}}$	$\frac{X'_{7.3}}{Q_{7.3}}$	$\frac{X'_{7.4}}{Q_{7.4}}$	$\frac{X'_{7.5}}{Q_{7.5}}$	$\frac{X'_{7.6}}{Q_{7.6}}$	$\frac{X'_{7.7}}{Q_{7.7}}$	1	$\frac{X'_{7.9}}{Q_{7.9}}$	1	1
$\frac{X'_{6.1}}{Q_{6.1}}$	$\frac{X'_{6.2}}{Q_{6.2}}$	$\frac{X'_{6.3}}{Q_{6.3}}$	$\frac{X'_{6.4}}{Q_{6.4}}$	$\frac{X'_{6.5}}{Q_{6.5}}$	$\frac{X'_{6.6}}{Q_{6.6}}$	1	1	$\frac{X'_{6.9}}{Q_{6.9}}$	1	1
$\frac{X'_{5.1}}{Q_{5.1}}$	$\frac{X'_{5.2}}{Q_{5.2}}$	$\frac{X'_{5.3}}{Q_{5.3}}$	$\frac{X'_{5.4}}{Q_{5.4}}$	$\frac{X'_{5.5}}{Q_{5.5}}$	1	1	1	$\frac{X'_{5.9}}{Q_{5.9}}$*	1	1
$\frac{X'_{4.1}}{Q_{4.1}}$	$\frac{X'_{4.2}}{Q_{4.2}}$	$\frac{X'_{4.3}}{Q_{4.3}}$	$\frac{X'_{4.4}}{Q_{4.4}}$	1	1	1	1	$\frac{X'_{4.9}}{Q_{4.9}}$*	1	1
$\frac{X'_{3.1}}{Q_{3.1}}$	$\frac{X'_{3.2}}{Q_{3.2}}$	$\frac{X'_{3.3}}{Q_{3.3}}$	1	1	1	1	1	$\frac{X'_{3.9}}{Q_{3.9}}$*	1	1
1	1	1	1	1	1	1	1	1	1	1
1	1	1	1	1	1	1	1	1	1	1

* *It seems doubtful if these are of much importance since $P_{5.9}$, $P_{4.9}$ and $P_{3.9}$ are small and probably zero.*

adults. (This latter assumption is strictly true, except for a very brief period during which a new adult is emerging from the pupal skin.) These assumptions may be introduced into the formulas by writing $P_{i,j}=0$, where $j>i$, (except $j=9$), and $P_{i,10}$, $P_{i,11}=0$ for all values of i. It is also evident that, of necessity, as flour, eggs and pupae cannot eat, all P's of the forms $P_{1,j}$, $P_{2,j}$ and $P_{9,j}$ are zero.

The C's may now be evaluated by an extension of the reasoning used in Equations 19 to 24. As such symbols as $\frac{X'_{i,j}}{P_{i,j}Y'_{i,j}}$ occur frequently, they will be written as $\frac{X'_{i,j}}{Q_{i,j}}$.

Certain of these are of no importance, namely, those for which $P_{i,j}=0$. Such a case gives, of course, the indeterminate form $\frac{0}{0}$, but it is easy to see that this reduces to the value 1. There result, then, the ratios shown in Table VIII, all equal. Those for which $P_{i,j}=0$ have been written as 1 immediately, and thus disposed of.

As, (See Equation 20)

$$E_iN_i=\sum_{j=1}^{j=11*}X'_{i,j},$$

and as any one of the X's may be obtained in terms of any other in the same row by means of the relationship

$$X'_{i,j}=\frac{X'_{i,h}Q_{i,j}}{Q_{i,h}}, \tag{36}$$

on substitution,

$$E_iN_i=\frac{X'_{i,h}}{Q_{i,h}}\sum_{j=1}^{j=11}Q_{i,j}, \tag{37}$$

whence

$$X'_{i,h}=\frac{E_iN_iQ_{i,h}}{\sum_{j=1}^{j=11}Q_{i,j}}, \tag{38}$$

which, on dividing by W_hA_h, becomes

$$C'_{i,h}=\frac{E_iN_iQ_{i,h}}{W_hA_h\sum_{j=1}^{j=11}Q_{i,j}}. \tag{39}$$

It is now necessary to consider the forms of the Q's. Some are equal to zero directly, and are thus of no further interest. These are Q's of the forms $Q_{1,j}$, $Q_{2,j}$, $Q_{9,j}$, $Q_{i,j}$ where $i<j$ (except $j=9$), and $Q_{i,10}$, $Q_{i,11}$ for all values of i. It must be remembered, of course, that any $Q_{i,j}$ is zero if N_i is zero.

As a preliminary step, the Q's may be divided into four classes, (a), (b) and (c) as on page 642, with an additional class (a_1) for encounters with flour. Thus remembering that $Q_{i,j}=P_{i,j}\ Y'_{i,j}$

*The summation may be made from 1 to 11 since $X'_{i,11}$ and $X'_{i,10}=0$.

Under case (a_1),

$$Q_{3.1} = \frac{P_{3.1}A_1W_1K_3\mu_3\pi r_{3.1}^2N_3G}{G}, \tag{40}$$

$$Q_{i.1} = \frac{P_{i.1}A_1W_1K_i\mu_i\pi r_{i.1}^2N_iG}{G}. \tag{41}$$

$$\vdots$$

$$Q_{11.1} = \frac{P_{11.1}A_1W_1K_{11}\mu_{11}\pi r_{11.1}^2N_{11}G}{G}. \tag{42}$$

Under case (a) there are formulas descriptive of amounts of assimilable material obtained by larvae or adults from eggs or pupae, thus

$$Q_{3.2} = \frac{P_{3.2}A_2W_2N_3N_2\mu_3\pi r_{3.2}^2}{G}, \tag{43}$$

$$Q_{4.2} = \frac{P_{4.2}A_2W_2N_4N_2\mu_4\pi r_{4.2}^2}{G}, \tag{44}$$

$$Q_{10.2} = \frac{P_{10.2}A_2W_2N_{10}N_2\mu_{10}\pi r_{10.2}^2}{G}, \tag{45}$$

$$Q_{6.9} = \frac{P_{6.9}A_9W_9N_6N_9\mu_6\pi r_{6.9}^2}{G}, \tag{46}$$

$$Q_{11.9} = \frac{P_{11.9}A_9W_9N_{11}N_9\mu_{11}\pi r_{11.9}^2}{G}. \tag{47}$$

Under case (b) there are formulas descriptive of amounts of assimilable material obtained from larvae of a given age by larvae of the same age, thus:

$$Q_{3.3} = \frac{4P_{3.3}A_3W_3N_3(N_3-1)\mu_3\pi r_{3.3}^2}{3G}, \tag{48}$$

$$Q_{4.4} = \frac{4P_{4.4}A_4W_4N_4(N_4-1)\mu_4\pi r_{4.4}^2}{3G}, \tag{49}$$

$$\vdots$$

$$Q_{i.i} = \frac{4P_{i.i}A_iW_iN_i(N_i-1)\mu_i\pi r_{i.i}^2}{3G}, \tag{50}$$

$$\vdots$$

$$Q_{8.8} = \frac{4P_{8.8}A_8W_8N_8(N_8-1)\mu_8\pi r_{8.8}^2}{3G}. \tag{51}$$

Under case (c) there are formulas descriptive of amounts of assimilable materials obtained from larvae of various ages, by larvae not of the same ages, and by adults, either mature or immature, thus:

$$Q_{4.3} = \frac{P_{4.3}A_3W_3N_4N_3F(\mu_4, \mu_3)\pi r_{4.3}^2}{G}, \tag{52}$$

$$Q_{5.3} = \frac{P_{5.3}A_3W_3N_5N_3F(\mu_5, \mu_3)\pi r_{5.3}^2}{G}, \tag{53}$$

$$Q_{11.6} = \frac{P_{11.6}A_6W_6N_{11}N_6F(\mu_{11}, \mu_6)\pi r_{11.6}^2}{G}. \tag{54}$$

The C''s may now be evaluated in terms of the Q's. The formulations may be simplified as a result of an examination of $F(\mu_i, \mu_j)$. It has been convenient hitherto to use the separate velocity corrections; it will now be shown that they may all be written in the form $F(\mu_i, \mu_j)$.

$$F(\mu_i, \mu_j) = \frac{1}{6\mu_i\mu_j}\left[-(|\mu_i-\mu_j|)^3+(\mu_i+\mu_j)^3\right]. \tag{55}$$

Suppose that $\mu_i > \mu_j$

Then if μ_i or μ_j is zero, while the other is not, clearly it must be $\mu_j = 0$.

Whence
$$F(\mu_i, \mu_j) = \frac{3\mu_i^2\mu_j-\mu_j^3}{3\mu_i\mu_j}. \tag{56}$$

Differentiating both numerator and denominator separately with respect to μ_j we obtain,

$$\frac{3\mu_i^2+3\mu_j^2}{3\mu_i^2}.$$

Whence
$$\lim_{\mu_j \to 0} F(\mu_i, \mu_j) = \mu_i.$$

Similarly it can be shown that where $\mu_j > \mu_i$,

$$\lim_{\mu_i \to 0} F(\mu_i, \mu_j) = \mu_j.$$

It is also evident from direct substitution in (55) that,

$$\lim_{\mu_i \to \mu_j} F(\mu_i, \mu_j) = \frac{4}{3}\mu_i \text{ (or } \frac{4}{3}\mu_j).$$

Whence, where $i = 3, 4, 5, \ldots 8, 10$ and 11,

$$C'_{i.1} = \frac{\dfrac{P_{i.1}W_1A_1K_iF(\mu_i,0)\pi r_{i.1}^2N_i^2G\,E_i}{G}}{W_1A_1\left[\dfrac{P_{i.1}W_1A_1K_iF(\mu_i,0)\pi r_{i.1}^2N_iG}{G}+\sum_{j=2}^{j=9}\dfrac{P_{i.j}W_jA_jF(\mu_i,\mu_j)\pi r_{i.j}^2N_iN_j}{G}\right]}, \tag{57}$$

$$C'_{i,1} = \frac{P_{i,1}K_iF(\mu_i, 0)\, r^2_{i,1}\, E_iN_iG}{P_{i,1}W_1A_1K_iF(\mu_i, 0)r^2_{i,1}G + \sum_{j=2}^{j=9} P_{i,j}W_jA_j\, F(\mu_i, \mu_j)r^2_{i,j}N_j} \tag{58}$$

and where $j = 2, 3, 4, \ldots .9$ and $j \neq i$

$$C'_{i,j} = \frac{P_{i,j}F(\mu_i, \mu_j)r^2_{i,j}N_iN_jE_i}{P_{i,1}W_1A_1K_iF(\mu_i, 0)\, r^2_{i,1}G + \sum_{k=2}^{k=9} P_{i,k}W_kA_k\, F(\mu_i, \mu_k)r^2_{i,k}N_k} \tag{59}$$

and where $j = i = 3, 4, 5, 6, 7, 8$, ($C'_{i,j} = 0$ when $i = 1, 2, 9$, or $j = 10$ or 11)

$$C'_{i,i} = \frac{P_{i,i}F(\mu_i, \mu_i)r^2_{i,i}\, N_i\, (N_i - 1)E_i}{P_{i,1}W_1A_1F(\mu_i, 0)r^2_{i,1}\, G + \sum_{k=2}^{k=9} P_{i,k}W_kA_k\, F(\mu_i, \mu_k)r^2_{i,k}N_k} \tag{60}$$

from which it is readily seen that $C'_{i,j}$ is zero if either N_i or N_j is zero.

Determination of the forms of the Z's

As stated above, Z_i is the rate at which a form with subscript $(i-1)$ is transforming to a form (i) at a time T.

Since the Z's involve certain functions the forms of which have not yet been determined, only a cursory explanation of the forms of the Z's will be given here, a more detailed explanation being reserved for later publication.

By an extension of notation previously given*, let $t_2, t_3 \ldots\ldots t_{11}$ be the fixed times at which transformation to the forms having subscripts 2, 3, 4, ...11 commences, *i.e.*, the first pupa comes into existence at t_2. Also let $\Gamma_2, \Gamma_3, \ldots\ldots \Gamma_{10}$ be the durations of individuals in the various life-history stages having subscripts from 2 to 10.†

It will be clear that the history of an adult, for example, reaching maturity at a time T may be summarized as follows: laid as an egg at $T - \sum_{2}^{10} \Gamma_i$; hatched to a first instar larva at $T - \sum_{3}^{10} \Gamma_i$; transformed to a second, third, fourth, fifth and sixth instar larva at the times, $T - \sum_{4}^{10} \Gamma_i$, $T - \sum_{5}^{10} \Gamma_i$, $T - \sum_{6}^{10} \Gamma_i$, $T - \sum_{7}^{10} \Gamma_i$, $T - \sum_{8}^{10} \Gamma_i$ respectively; pupated at $T - \Gamma_{10} - \Gamma_9$; emerged as an immature adult at $T - \Gamma_{10}$; and became mature at T. Thus with each individual there are associated past times at which its various transformations took place.

Consider two groups of eggs, α and β, one of which, α, hatches promptly at t_2, while the other hatches later. In the case of the first group, α, the depredations due to eating have been caused only by the N_{11} adults originally present at $T = t_2 = 0$, whereas in the case of the group β, in the early part of its

*As only first generation eggs will be discussed, we may write t_2, t_3, t_4, rather than $t_2(1)\ t_2(2)$ etc.

†Γ_{11} is indefinite, being the life of the mature adult, as such.

life as eggs it was attacked only by the N_{11} mature adults, while in the later part of its life it was attacked by both the N_{11} mature adults and the N_3 first instar larvae existing subsequent to the time t_3. It is thus apparent that any function embodying the rate at which this group, β, has been eaten at various times, must be discontinuous at t_3. If moreover, T be greater than t_{11}, discontinuities must also exist at such of the times t_3, t_3, ...t_{11} as fall within the time span over which the group has been in existence as a group of eggs. Similar discontinuities will occur in other functions embodying the rates of eating of other forms, and since the Z's are such functions, the above discontinuities will occur in the Z's as will be shown below. For reference the values of t_2 to t_{11} and of Γ_2 to Γ_{10} are given in Table IX, computed from Tables I and V.

TABLE IX

VALUES OF t_2 TO t_{11} AND Γ_2 TO Γ_{10} AT 27° C.

Γ	Value	t	Value	Derivation of t
Γ_2	6.04	t_2	0.00	$t_2=t_0=0$
Γ_3	2.43	t_3	6.04	$t_2+\Gamma_2$
Γ_4	3.63	t_4	8.47	$t_2+\Gamma_2+\Gamma_3$
Γ_5	3.03	t_5	12.10	$t_2+\Gamma_2+.....\Gamma_4$
Γ_6	3.27	t_6	15.13	$t_2+\Gamma_2+.....\Gamma_5$
Γ_7	3.39	t_7	18.40	$t_2+\Gamma_2+.....\Gamma_6$
Γ_8	6.67	t_8	21.74	$t_2+\Gamma_2+.....\Gamma_7$
Γ_9	8.64	t_9	28.46	$t_2+\Gamma_2+.....\Gamma_8$
Γ_{10}	6.04	t_{10}	37.10	$t_2+\Gamma_2+.....\Gamma_9$
		t_{11}	43.14	$t_2+\Gamma_2+.....\Gamma_{10}$

It has been shown (Equation 31) that

$$\lim_{T\to t_2=0}\frac{dN_2}{dT}=R\epsilon N_{11},$$

that is, eggs are coming into existence at this rate when $T=t_2=0$.

Consider the rate at which eggs are arriving at hatching age when $T=t_3$. Clearly this must be less than $R\epsilon N_{11}$ since many eggs have been eaten.

Let this rate be $\theta(t_3)$.

Then the total reduction from the rate at which eggs were coming into existence at $T=t_2=0$ to the rate at which they are arriving at hatching age at t_3 is $R\epsilon N_{11}-\theta(t_3)$.

But the rate of eating of a small group of eggs laid between $T=t$ and $T=t+dt$ is, at any time t,

$$\frac{\theta(t)C'_{11.2}}{N_2}\,dt,$$

whence

$$\theta(t_3)=R\epsilon N_{11}-\int_{t_2}^{t_3}\frac{\theta(t)C'_{11.2}}{N_2}\,dt. \tag{61}$$

When $T=t_3$, first instar larvae (subscript 3) are present, whence during a sufficiently small neighborhood where $T>t_3$

$$\theta(T)=R\epsilon N_{11}-\int_{T-\Gamma_3}^{t_3}\frac{\theta(t)C'_{11.2}}{N_2}\,dt-\int_{t_3}^{T}\frac{\theta(t)\left(C'_{11.2}+C'_{3.2}\right)}{N_2}\,dt. \tag{62}$$

From Table IX it will be seen that $t_3=6.04$ and that $t_4=8.47$, whence, as $\Gamma_2=6.04$ and $\Gamma_3=2.43$, it is possible for T to exceed t_4 without $T-\Gamma_3$

exceeding t_3. In such a case, fourth instar larvae are present during the period from t_4 to T and we have

$$\theta(T) = R\epsilon N_{11} - \int_{T-\Gamma_2}^{t_3} \frac{\theta(t)C'_{11.2}}{N_2}\,dt - \int_{t_3}^{t_4} \frac{\theta(t)\left(C'_{11.2}+C'_{3.2}\right)}{N_2}\,dt - \int_{t_4}^{T} \frac{\theta(t)\left(C'_{11.2}+C'_{4.2}+C'_{3.2}\right)}{N_2}\,dt. \tag{63}$$

When $T=12.08$, $T-\Gamma_2=t_3$ and the first integral on the right hand of Equation 63 becomes zero, since the upper and lower limits are equal.

When T becomes greater than 12.08, $T-\Gamma_2$ becomes greater than t_3 so that the integral becomes negative. Since this has no connection with any real case in an actual population, the fact that only positive integrals are to be considered will be denoted by a plus sign, thus: $\overset{+}{\int}$.

As for a sufficiently small neighborhood, $T>12.08$

$$\theta(T) = R\epsilon N_{11} - \overset{+}{\int_{T-\Gamma_2}^{t_4}} \frac{\theta(t)\left(C'_{11.2}+C'_{3.2}\right)}{N_2}\,dt - \overset{+}{\int_{t_4}^{T}} \frac{\theta(t)\left(C'_{11.2}+C'_{4.2}+C'_{3.2}\right)}{N_2}\,dt. \tag{64}$$

It is seen that as T increases, there is a periodic addition of integrals on the right hand, and a concomitant extinction of integrals on the left, accompanied by a migration of the lower limit $T-\Gamma_2$. This migration will be denoted by an arrow, thus: $\overset{+}{\underset{T-\Gamma_2}{\int}}$.

Whence, for a value of T greater than say t_i where t_i is any one of the t's

$$\theta(T) = R\epsilon N_{11} - \overset{+}{\underset{T-\Gamma_2}{\int}}^{t_3} \frac{\theta(t)C'_{11.2}}{N_2}\,dt - \overset{+}{\int_{t_3}^{t_4}} \frac{\theta(t)\left(C'_{11.2}+C'_{3.2}\right)}{N_2}\,dt$$

$$- \overset{+}{\int_{t_4}^{t_5}} \frac{\theta(t)\left(C'_{11.2}+\sum_{j=3}^{j=4} C'_{j.2}\right)}{N_2}\,dt - \cdots\cdots\cdots - \overset{+}{\int_{t_i}^{T}} \frac{\theta(t)\left(C'_{11.2}+\sum_{j=3}^{j=i} C'_{j.2}\right)}{N_2}\,dt, \tag{65}$$

which may be written in contracted form as

$$\theta(T) = R\epsilon N_{11} - \overset{+}{\underset{T-\Gamma_2}{\int}}^{t_3} \frac{\theta(t)\,C'_{11.2}}{N_2}\,dt - \sum_{k=3}^{k=i-1} \overset{+}{\int_{t_k}^{t_{k+1}}} \frac{\theta(t)\left(C'_{11.2}+\sum_{j=3}^{j=k} C'_{j.2}\right)}{N_2}\,dt$$

$$- \overset{+}{\int_{t_i}^{T}} \frac{\theta(t)\left(C'_{11.2}+\sum_{j=3}^{j=i} C'_{j.2}\right)}{N_2}\,dt. \tag{66}$$

It will be apparent that similar functions may be written for the rates of transformation from first instar to second, etc., but as little is known as yet as to the form of the function $\theta(t)$ these formulations will not be included here.

The egg and larval populations for a sufficiently small neighborhood, $T > t_3$

When an egg hatches, the larva is at first comparatively inactive, and as the only material lost during the transformation from egg to first instar larva is the minute amount which makes up the shell, during a sufficiently small neighborhood, $T > t_3$, first instar larvae may be thought of as eggs. In this case it will at once be apparent that the sum of the two populations, eggs and first instar larvae, will be equal to what the egg population alone would have been, in the absence of hatching, with the exception of those eggs which entirely pass out of existence owing to natural mortality at hatching. That is to say, if $\bar{N}_2$ be the value which the egg population would have reached at a time T, in the absence of hatching, and if N_2 and N_3 are the actual numbers of eggs and first instar larvae, at any such time,

$$\bar{N}_2 - (1 - U_3)Z_3 = N_2 + N_3. \tag{67}$$

If now, as is the case, $(1 - U_3)$ be small, for a short time after hatching commences, two situations may arise:

(a) The egg population has reached a point of quasi-equilibrium, *i.e.*, is oscillating between the greatest integral number less than ξ and the least integer greater than ξ (see Equation 30). In this case as $N'_3 > 0$ when $T > t_3$, N'_2 will become negative as soon as $T > t_3$.

(b) Such a condition of quasi-equilibrium has not been reached by the egg population when $T = t_3$. In this case, the egg population will continue to increase until such a value is reached that

$$R\epsilon N_{11} = Z_3 + \sum_{i=3}^{i=k} C'_{i.2} + C'_{11.2}, \tag{68}$$

where k is the subscript for the oldest larva present at the time that the value of N_2 in Equation 68 is reached. After this time, the egg population decreases. Inactivity of first instar larvae is not necessary to the truth of the above expression however.

It seems hardly necessary to point out that immediately subsequent to $T = t_3$, the expression

$$U_3 Z_3 > \sum_{i=3}^{i=k} C'_{i.3} + C'_{11.3}$$

must be satisfied if the larval population is ever to come into existence at all.

The question might now be asked as to what would occur should transformation to second instar larvae, (subscript 4) not take place. So far the writer has not been able to determine this point mathematically, but it would seem that there are two possibilities:

(c) The egg and larval populations come into stable equilibrium, in which the rate of egg transformation to first instar larvae $U_3(Z_3)$ at all times balances

the larval loss due to natural death, and due to the eating of larvae by larvae and adults, and in which Z_3, and the eating of eggs, and the death of eggs are together equal to $R\epsilon N_{11}$. That is, N_2' and N_3' are zero.

(d) The egg and first instar larval populations enter into an infinite series of "cyclical" changes, where by "cyclical" it is not necessarily meant that each cycle is identical with the preceding one, but is nevertheless of the same general form.

It is felt, lacking rigorous mathematical proof, that (c) can be ruled out for the following reason. At any time T the rate of production of first instar larvae is a function of all the past history of the egg and larval populations during a period of time from $T-\Gamma_2$ to T, that is to say,

$$U_3Z_3 = U_3\left[R\epsilon N_{11} - \int_{T-\Gamma_2}^{T} \theta(t)\left(\frac{C'_{3.2}+C'_{11.2}}{N_2}\right)dt\right], \text{ etc.} \tag{69}$$

Suppose that N_2 and N_3 have just arrived at such a pair of values that

$$U_3Z_3 = C'_{3.3}+C'_{11.3}, \tag{70}$$

i.e., the equilibrium mentioned under case (a) is attained. Let T receive a finite increment ΔT, then,

$$U_3Z_3 = U_3\left[R\epsilon N_{11} - \int_{T+\Delta T-\Gamma_2}^{T+\Delta T} \theta(t)\left(\frac{C'_{3.2}+C'_{11.2}}{N_2}\right)dt\right] \tag{71}$$

Then if U_3Z_3 still equals $C'_{3.3}+C'_{11.3}$, N_2 and N_3 must have had the values mentioned above throughout the interval $T-\Gamma_2$ to T, whence the above equilibrium cannot be maintained for a finite time unless it has already been maintained for a period Γ_2. Since N_2 and N_3 are not at these equilibrium values when $T=t_3$, they can never, on attaining them, remain at them for a finite time. It follows that where $Z_4=0$, *i.e.*, where no transformations to second instar larvae occur, the first instar larvae increase in numbers until

$$U_3Z_3 = C'_{3.3}+C'_{11.3},$$

and then, due to eating, decrease again. A second such maximum cannot occur again until a period of at least Γ_2 has passed, for not until then can the increase in egg population (resulting from a decrease in $C'_{3.2}$) have any major effect upon the larval population.

It is true, of course, that there will be a retardation in the rate of decrease of N_3 due to the increase in Z_3 with decrease in $C'_{3.2}$ but this cannot in general make $N_3'>0$.

Generally speaking, where $Z_4>0$, the above-mentioned maximum value of the first instar larvae is not attained, owing to the reduction caused by Z_4.

It is believed that the other larval instars increase in numbers, tending towards analogous maxima, and in general, decrease in numbers before reaching them, for analogous reasons.

Distribution by ages in the total larval population

During actual counts of larval populations which had been running for some time, it was noticed that there was an increase in the proportion of older larvae, even after the time when larvae of all stages were present. That is to say, with older populations the distribution by ages tends to become increasingly skew in the direction of the greatest age. The explanation of this phenomenon from the theory thus far developed is comparatively simple.

Consider a group of first instar larvae hatching from eggs during a period $t_0 < T < t_0 + \Delta t$, where Δt is some small increment of time. By reason of the postulate that $C'_{i,j} = 0$, $i < j$ except $j = 9$, all through their lives this small group is subjected to an "eating force" of only $C'_{j,j} + C'_{11,j}$, where j is the subscript indicative of the instar in which the group exists at any time. On the other hand, a similar group hatching out over a period of equal duration, but situated later in time, when there are perhaps larvae of the second and third instars present, will be subject to much greater eating, namely, $C'_{(j+2),j} + C'_{(j+1),j} + C'_{j,j} + C'_{11,j}$. Not only this, but the group will be smaller to start with, since it is easily seen that in populations of the type described in this paper $\frac{\partial Z_i}{\partial T} < 0$ where i is the subscript of any larval instar. Thus, theoretically at least, the first larva hatching promptly at $T = t_0$ will always pupate, provided it is not eaten by an adult, and does not die from some natural cause. Obviously then, with the passage of time, all but the older larvae tend to disappear, and the age distribution is skewed in the direction of the greatest age.

Pupal populations

In general it may be said that the pupal populations tend, as do the larval populations, to reach a maximum value, at which the increase due to transformation from sixth instar larvae (subscript 8) just balances the loss by natural death and by eating, but do not attain this value by reason of transformation to the adult form.

Adult populations, $T > t_{10}$

The equation descriptive of the growth of the adult population is in general far simpler than those descriptive of the growths of the egg, larval and pupal populations owing to the fact that $C'_{i,10}, C_{i,11} = 0$.

Therefore, the only negative term will be one to account for the slow and gradual death of adults by reason of sheer accident and infirmity. This term may be written in the form $\overline{K}\ (T - t_{11})$ where $\overline{K}$ is a constant.

What then limits the size of the adult population? The equation may be written as

$$N_{11} = Z_{11} - \overline{K}(T - t_{11}), \tag{72}$$

whence it is at once seen that the limiting factor, since $\overline{K}$ is very small, is a diminution in Z_{11}, the rate of transformation from immature to mature adults. Thus, if $\overline{K}$ be considered as practically negligible, N_{11} will increase until $Z_{11} = 0$ which practically, as $C'_{i,10} = 0$, means $Z_{10} = 0$.

An interesting point arises here. Suppose that Y adults, mature and immature, are sufficient to reduce and hold the pupal population practically at zero, so that N'_{10} is zero. By reason of the fact that some time is necessary to eliminate the pupal population in existence at $T=t_{10}$ the adult population generally rises above the value Y which would obtain under any particular set of environmental conditions (temperature, flour mass, etc.) As this large adult population cannot reduce the pupal population to less than zero, it feeds upon flour, eggs, and such larvae as emerge from time to time, and in the meantime dwindles slowly away (see Figs. 4 and 5) by reason of the second term in Equation 72, to approach the value Y from above.

Owing to unavoidable failure in the mechanical equipment used to maintain constant temperatures, no populations were grown for a sufficient length of time to determine what would happen beyond this point, but in the case of some populations in which the number of adults was accidentally greatly reduced, a new cycle analogous with those mentioned on page 660 commenced, the adult population rising again to a value in excess of Y. It is believed that a periodic fluctuation with a period of $t_e+\dfrac{\bar{N}_{11}-Y}{\bar{K}}$ would be set up, where $\bar{N}_{11}$ is the maximum number of adults reached under any particular set of conditions, and t_e is the time from t_2 to the time of reaching the maximum number of adults.

It might also be asked how hatching of eggs can fail to occur, as it at times does, when subsequent to $T=S$ there are perhaps 1000 eggs present. The answer to this lies in the fact that Z_3 is dependent not only upon the number of eggs, but also on the rates of consumption of the same throughout their life as eggs. In a case such as the above, the rates of consumption are such that the probability that an egg will be found and eaten in a time less than Γ_2 is 1. Hence no eggs survive long enough to hatch, even though they are very numerous. Such a condition is of course unstable, in that a diminution of larvae or other predators will cause an immediate increase in the numbers of first instar larvae.

The Protective Influence of One Form on Another, in the Matter of Eating

Consider the addition of a new form to the system at any time. It will be apparent that if this new form is edible, it must bear some of the depredations of the predators, and for that reason must diminish to some extent the rate at which all other edible forms are consumed. The mechanism of this, mathematically, is quite simple, as it operates through the fact that the addition of a new edible form adds another Q to the denominator of all the C''s already in operation, and since the added quantity is real and positive, the C''s are thereby diminished. If it should occur that the added form is predatory as well as edible, the protection offered may be more than offset by the additional predatory influence. This will of course depend on the relative value of the new C' introduced and the diminution in those already present.

This matter will be referred to more extensively in Part 3.

Part 3

Discussion of Experimental Data

In Tables X, XI, XII and XIII are tabulated the actual population counts from duplicate experiments at four temperatures, namely, 17°, 22°, 27°, and 32°C. all at 75% relative humidity. (This was somewhat exceeded in the cases of the two populations at the lower temperatures owing to unavoidable condensation on the cooling coils in the controlled cabinets.) The duplicate experiments are denoted as (A) and (B). The mean values from (A) and (B) are also shown.

These means are plotted as Figs. 2, 4, 6 and 8, while Figs. 3, 5, 7 and 9 show curves drawn on a basis of the actual data, but with modifications made in an endeavor to replace information lost by reason of the relative infrequency of the counts. These changes have been made on the basis of the information gained from the theory developed in Part 2. Care has been taken to make

TABLE X*

POPULATION SERIES IN WHOLE WHEAT FLOUR, 32 GM., AT 17°C. AND 75% RELATIVE HUMIDITY

Time, days	Eggs (A)	Eggs (B)	Eggs Mean	Larv. (A)	Larv. (B)	Larv. Mean	Ad. (A)	Ad. (B)	Ad. Mean	Tot. (A)	Tot. (B)	Tot. Mean
0	16						16	16	16	16	16	16
10	41	24	37				16	16	16	57	40	48
20	61	47	54				16	16	16	77	63	70
30	102	93	97				16	16	16	118	109	113
40	134	112	123				16	16	16	150	128	139
50	162	141	152				16	16	16	178	157	167
60	186	160	173	2		1	16	16	16	204	176	190
70	178	153	165	1		.5	16	16	16	195	168	182
80	219	143	181	3	2	2.5	16	16	16	248	161	204
90	245	130	187	5	0	2.5	16	15	15.5	266	145	205
100	253	149	201	5	3	4	16	15	15.5	274	167	220
110	249	168	208	4	0	2	16	15	15.5	269	183	226
120	214	169	191	13	1	7	16	15	15.5	243	185	191
130	222	168	195	13	1	7	16	15	15.5	251	184	217
140	309	189	249	14	0	7	15	15	15	338	204	271
150	275	203	239	12	0	6	15	15	15	302	208	255
160	190	186	188	8	0	4	15	15	15	213	201	207
170	212	213	212	8	5	6	15	15	15	235	243	239
180	203	220	211	6	5	5	15	15	15	224	240	232
190	243	265	254	8	3	5	15	15	15	266	283	274
200	258	230	244	15	9	12	15	15	15	288	254	271
210	219	245	232	16	19	17	15	15	15	250	269	259
220	210	224	217	31	39	35	15	15	15	256	278	267
230	261	233	247	32	32	32	15	15	15	308	280	294
240	221	201	211	8	57	32	15	15	15	244	273	258
250	229	190	209	20	82	51	15	15	15	304	287	295
260†	...	...	...	...	...	....	...	...	....	...	...	...
270	234	174	204	42	138	90	15	15	15	291	327	309
280	219	149	184	40	95	67	15	15	15	274	259	266

* *The writer is indebted to Dr. R. N. Chapman for the data in this table.*

† *Count missed on this day.*

NOTE:—*No pupation occurred at* 17°C.

only such modifications as could be found homologously at all temperatures with the exception of 17°C., in which case, owing to the great value of Γ_2 only the earliest stages of the population growth are manifest.

As soon as T becomes greater than $t_2=0$, eggs commence to accumulate according to Equation 29, and as has been shown, tend towards the limiting value ξ, at which point they are found and eaten as rapidly as they are laid. At 17°C., owing to the high value of Γ_2, this condition is practically attained, but as at times, a few eggs do hatch, in the region of 60 to 70 days, Fig. 3,

$$N'_2=R\epsilon N_{11}-Z_3-C'_{3.2}-C'_{11.2}<0. \tag{73}$$

At 22°, 27°, and 32°C. this equilibrium value ξ is not reached owing to the reduced value of Γ_2, and at p_1 the egg population reaches a maximum as described in Equation 68, and then decreases owing to hatching to form first instar larvae.

Thus, the population at 17°C. is an example of Case (a) page 659 while the other three populations illustrate Case (b), page 659.

TABLE XI*

POPULATION SERIES IN WHOLE WHEAT FLOUR, 32 GM., AT 22°C. AND 75% RELATIVE HUMIDITY

Time, days	Eggs (A)	Eggs (B)	Eggs Mean	Larv. (A)	Larv. (B)	Larv. Mean	Pup. (A)	Pup. (B)	Pup. Mean	Ad. (A)	Ad. (B)	Ad. Mean	Tot. (A)	Tot. (B)	Tot. Mean
0										16	16	16	16	16	16
10	196	222	209	11	12	11				16	16	16	223	250	236
20	338	314	326	79	661	70				16	16	16	433	391	414
30	399	383	391	210	131	170				16	16	16	625	530	577
40	371	398	384	323	219	271	0	0	0	16	16	16	710	633	671
50	287	281	284	315	204	259	1	3	2	16	16	16	619	504	561
60	225	186	205	365	326	345	7	9	8	16	19	17	613	440	526
70	200	149	174	372	248	310	22	22	22	19	26	22	613	445	529
80	132	118	125	297	153	225	97	45	71	27	35	31	553	356	454
90	79	124	101	175	176	175	93	81	87	76	59	62	423	440	431
100	106	159	132	92	129	110	57	74	65	114	83	98	369	445	407
110	161	243	202	47	82	64	10	58	34	136	124	130	354	507	430
120	157	351	254	45	83	64	2	37	19	130	142	136	334	613	473
130	128	347	237	69	176	122	2	9	5	120	148	134	319	680	499
140	151	325	238	72	131	101	0	2	1	109	140	124	325	598	461
150	148	235	191	77	155	116	0	0	0	101	137	119	326	527	426
160	87	158	122	67	162	114	0	0	0	92	128	110	246	448	347
170	250	382	316	37	167	102	0	0	0	87	120	103	374	669	521
180	621	610	615	52	122	87	0	0	0	86	119	102	759	851	805
190	487	336	411	207	201	204	1	1	1	80	121	100	774	659	716
200	377	224	300	248	182	215	0	1	1	76	118	97	701	525	603
210	224	134	179	346	201	273	0	5	2	71	114	92	641	454	547
220	144	65	104	328	184	256	0	9	4	69	106	87	541	364	447
230	83	49	66	307	148	227	6	2	4	63	88	75	409	287	348
240	50	37	43	279	96	187	13	0	6	62	80	71	404	213	308
250	54	34	44	263	59	161	7	1	4	60	64	62	384	158	271
260	268	158	218	155	23	89	0	0	0	56	55	55	479	236	857
270	284	554	419	230	44	137	0	0	0	55	48	51	669	646	657
280	521	580	550	300	202	251	0	0	0	55	46	50	876	828	852

* *The writer is indebted to Dr. R. N. Chapman for the data in this table.*

The writer confesses inability to explain the sudden fall in larval population at p_2 in the case of the population grown at 22°C. Lacking knowledge of the value of the Γ's for 22°C., it is not possible to determine whether this is an inherent peculiarity of the population growth or whether it is due to faulty technique. It is possible that it is due to relatively great activity on the part of sixth instar larvae at this temperature, but this is hardly in accord with observations made of such larvae. Moreover, such activity would manifest itself in an even sharper decline in egg population. Again, had such a decrease in the larval population actually occurred, it would have been reflected in a similar drop in pupal population at a time Γ_8 later. As there is no evidence of this, beyond the fact that the pupal curve seems somewhat bluntly truncated at 90 days, the time of the expected discrepancy, it is assumed that it is due to an error in count of an even hundred in "B" at 50 days, the finely waved line indicating the appropriate correction.

T now increases to approach and exceed t_9, and as pupae make their appearance,

$$N'_9 = U_9 Z_9 - \sum_{i=3}^{i=8} C'_{i,9} - C'_{11,9} > 0. \tag{74}$$

TABLE XII*

POPULATION SERIES IN WHOLE WHEAT FLOUR, 32 GM., AT 27°C. AND 75% RELATIVE HUMIDITY

Time, days	Eggs (A)	Eggs (B)	Eggs Mean	Larv. (A)	Larv. (B)	Larv. Mean	Pup. (A)	Pup. (B)	Pup. Mean	Ad. (A)	Ad. (B)	Ad. Mean	Tot. (A)	Tot. (B)	Tot. Mean
0										16	16	16	16	16	16
10	363	383	373	18	51	34				15	17	16	396	451	423
20	350	299	324	319	316	317		1	1	14	17	15	669	633	651
25	213	227	220	377	388	382	2	6	4	13	16	14	605	637	621
30	149	143	146	365	403	384	7	14	10	13	17	15	534	577	555
35	259	261	260	309	308	308	56	73	64	19	24	21	643	666	654
40	202	225	213	261	288	274	171	171	171	26	46	36	660	730	695
46	331	229	280	157	183	170	138	133	135	161	173	167	779	718	748
50	341	218	279	128	159	143	69	90	79	229	236	232	767	703	735
55	334	332	333	144	142	143	26	27	26	272	292	282	776	793	784
60	328	331	329	104	137	120	118	21	19	285	304	294	735	793	789
70	428	327	377	41	87	64	24	39	31	299	333	316	792	786	789
80	522	492	507	12	30	21	17	27	22	308	356	332	859	905	882
90	706	869	782	10	3	6	3	27	15	303	365	334	1022	1264	1143
100	824	1040	932	49	36	42	4	1	2	317	371	344	1194	1448	1321
110	812	750	781	73	109	91	1	1	1	297	367	332	1183	1227	1305
120	509	615	562	221	157	189	15	15	15	316	374	345	961	1097	1029
130	388	460	424	107	100	103	27	40	33	321	384	352	843	984	913
140	491	717	604	92	64	78	16	35	25	325	390	357	924	1206	1065
150	323	681	502	75	47	61	18	14	16	323	405	364	739	1147	943
160	216	274	245	73	98	85	14	8	11	332	416	374	635	796	715
170	372	446	409	59	74	66	2	12	7	326	412	369	759	944	851
180	138	110	124	30	57	43	0	13	6	319	401	360	487	581	534
190†	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....

* *The writer is indebted to Dr. R. N. Chapman for the data in this table.*

† *Population accidentally killed at 190 days by escape of ammonia from refrigeration equipment.*

This pupal population tends to increase to such a point that,

$$U_9Z_9=\sum_{i=3}^{i=8}C'_{i.9}-C'_{11.9}, \tag{75}$$

but by reason of transformation to immature adults, arrives only at the maximum at p_7 where

$$U_9Z_9=\sum_{i=3}^{i=8}C'_{i.9}-C'_{11.9}-C'_{10.9}-Z_{10}. \tag{76}$$

The larval population continues to increase subsequent to $T=t_0$, for a short period, reaching a maximum at p_3 where

$$N'_L=U_3Z_3-Z_9-\sum_{i=j}^{i=11}\sum_{j=3}^{i=8}C_{i.j}=0^* \tag{77}$$

Subsequent to $T=t_0$ and also to the time of p_3, the egg population continues to fall, to reach a minimum where,

$$N'_2=R_eN_{11}-Z_3-\sum_{i=3}^{i=8}C'_{i.2}-C'_{11.2}. \tag{78}$$

TABLE XIII†

POPULATION SERIES IN WHOLE WHEAT FLOUR, 32 GM., AT 32°C. AND 75% RELATIVE HUMIDITY

Time, days	Eggs (A)	Eggs (B)	Eggs Mean	Larv. (A)	Larv. (B)	Larv. Mean	Pup. (A)	Pup. (B)	Pup. Mean	Ad. (A)	Ad. (B)	Ad. Mean	Tot. (A)	Tot. (B)	Tot. Mean
0										16	16	16	16	16	16
10	344	366	355	182	213	197	0	0	0	15	16	15	541	595	568
20	115	100	107	423	457	440	3	0	1	14	15	14	555	572	563
25	129	106	117	274	281	277	110	131	120	15	14	14	528	532	530
30	127	172	149	122	130	126	216	241	228	89	96	92	554	639	596
35	446	270	358	93	118	105	117	87	102	231	307	264	887	882	884
40	358	257	307	56	83	69	26	19	22	343	358	350	783	737	760
46	381	352	366	46	67	56	3	13	8	352	366	359	782	798	790
50	390	375	382	44	40	42	2	7	4	357	368	362	793	790	791
60	465	456	460	4	7	5	4	5	5	376	371	373	849	839	844
70	711	669	690	4	7	7	0	0	0	362	363	362	1077	1036	1056
80	837	687	762	17	6	11	0	1	1	358	371	364	1212	1065	1138
90	993	838	915	13	5	9	0	0	0	361	362	361	1367	1205	1286
100	940	925	932	11	6	8	2	1	1	353	361	357	1306	1293	1299
110	1263	963	1113	55	35	45	1	1	1	341	359	350	1658	1338	1498
120	744	559	651	139	42	90	3	2	2	341	360	350	1227	963	1095
130	448	738	593	106	33	119	10	2	6	332	355	343	896	1128	1013
140	765	906	835	58	25	41	14	9	12	315	335	325	1152	1275	1213
150	890	573	731	37	134	85	1	1	1	315	323	319	1243	1031	1137
160	653	280	466	69	91	80	0	22	11	307	288	297	1026	681	853
170	614	497	555	87	23	55	0	2	1	284	260	272	985	782	883
180	919	1032	975	122	260	191	0	0	0	279	254	266	1320	1546	1433
190	515	190	352	151	333	242	2	0	1	257	225	241	925	748	836
200	506	187	346	106	238	172	5	67	36	214	204	209	831	696	763

† *The writer is indebted to Dr. R. N. Chapman for the data in this table.*
NOTE:—*Population accidentally destroyed by failure of temperature control, at 203 days.*
* *Note that* $N_{10}=0$ *and that* $C'_{9.j}=0$.

and then, by reason of reduction in the numbers of the highly predatory sixth instar larvae (subscript 8), and by reason of the protective influence of the edible pupae (see page 662), acting as an alternative food for the remaining predators, N'_2 becomes greater than zero, and the egg population again increases.

In the case of the population grown at 22°C. there is an additional refutation of the idea that sixth instar larvae grown at 22°C. are highly predatory as the diminution of their numbers does not decrease the rate of eating of eggs sufficiently to cause a great rise in the egg population. Possibly such a rise did occur, and was missed on account of the comparative infrequency of counts. It is an unavoidable misfortune that no count was made at 65 days.

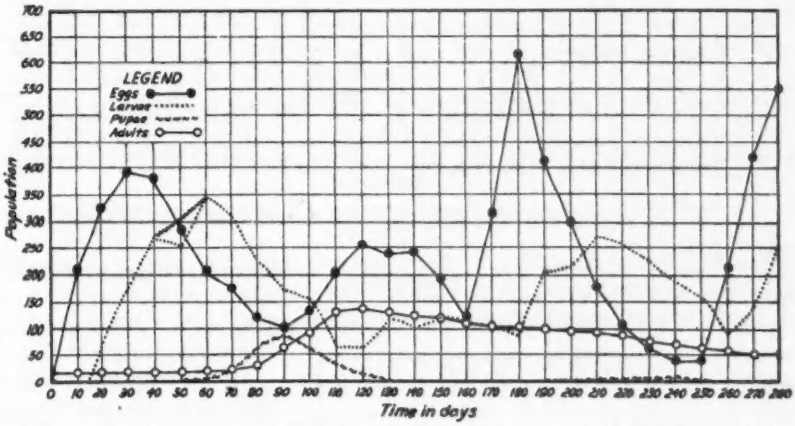


FIG. 4. *Population growth of T. confusum, Duv. at 22°C., mean of (A) and (B) populations.*

T now increases to approach and exceed t_{10} when immature adults (subscript 10) begin to come into existence. For a short time subsequent to t_{10} the egg population continues to increase, until with increase in N_{10} a maximum is reached at p_8 where,

$$N'_2 = R\epsilon N_{11} - Z_3 - \sum_{i=3}^{i=8} C'_{i.2} - C'_{10.2} - C'_{11.2}. \tag{79}$$

Subsequent to this time, for the same reasons, N'_2 becomes less than zero, and the egg population falls to reach a minimum at p_8 which will be discussed later.

In the meantime, subsequent to t_{10}, the pupal population continues to increase until a maximum is reached at p_7, due to increase in Z_{10}. The writer is unable to say whether Z_{10} is increasing or decreasing at this time. However, at p_7, Equation 76 must hold. Immediately subsequent to p_7, N'_9 becomes negative by a continuation of the reasoning set forth in the above paragraph.

During the period subsequent to t_9, the protective influence of the pupae and the progressive diminution in Z_{10} produce a slight increase in the rate of increase of larvae in general.

To return to a consideration of p_6: the reversal of the sign of the derivative N'_2 is due to transformation of the predatory but non-egg-laying immature adults into predatory but egg-laying mature adults. Thus by the operation

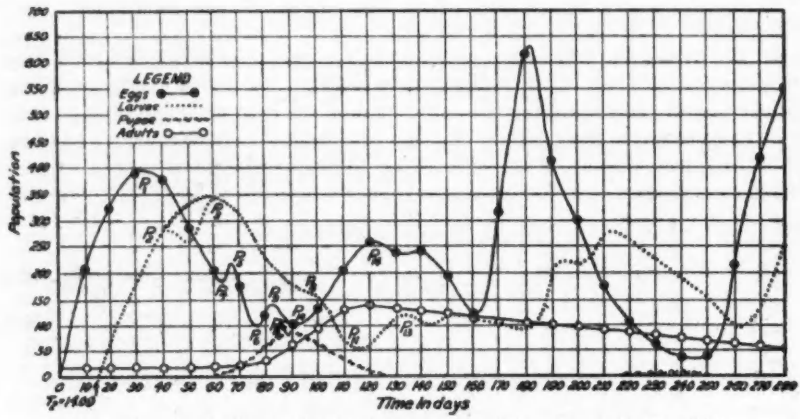


FIG. 5. *Smoothed curves for population growth of T. confusum, Duv. at 22°C.*

of Z_{11}, the function descriptive of the rate of this transformation, N_{11} is greatly increased, and thus $R \epsilon N_{11}$ is increased. This results in an increase in N'_2, so that it becomes greater than zero, and the egg population rises to reach a maximum again at p_9.

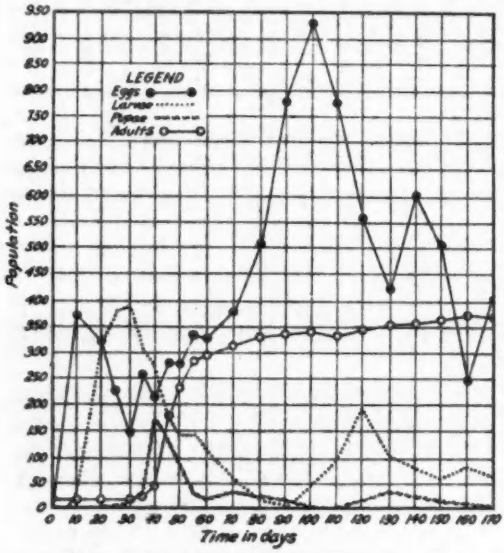


FIG. 6. *Population growth of T. confusum, Duv. at 27°C., mean of (A) and (B) populations.*

This further arrest in the increase in the number of eggs is due to the withdrawal of pupae as an alternative food for the predators subsequent to p_8. A similar reduction in the numbers of larvae is seen immediately subsequent to p_8.

Subsequent to p_9, by the continued operation of this factor, N'_2 again becomes negative, and the egg population falls to another minimum at p_{10}, where, by reason of the continued increase in N_{11}, the sign is again reversed.

Subsequent to p_{10}, the egg production increases

enormously, and here again the protective influence of an alternative food is seen, as before any sensible increase in the rate of hatching can take place, an increase in the larval population is seen at p_{11}.

This effect upon the larvae is in turn reflected in a slight reduction in N'_2 as seen at p_{12} (p_{12} is not clearly defined at 22°C. owing to slight larval activity at this temperature) following which the egg population continues to increase.

During this enormous rise in the egg population, although C''s of the form $C'_{i,2}$ are very great, not all eggs can be consumed by the adults and the comparatively small larval populations before the eggs have reached an age Γ_2. Hence some hatching does occur to cause an increase in the larval population at p_{13}. This increase in turn so augments the predatory population as to again reverse the sign of N'_2 and decrease the egg population subsequent to p_{14}.

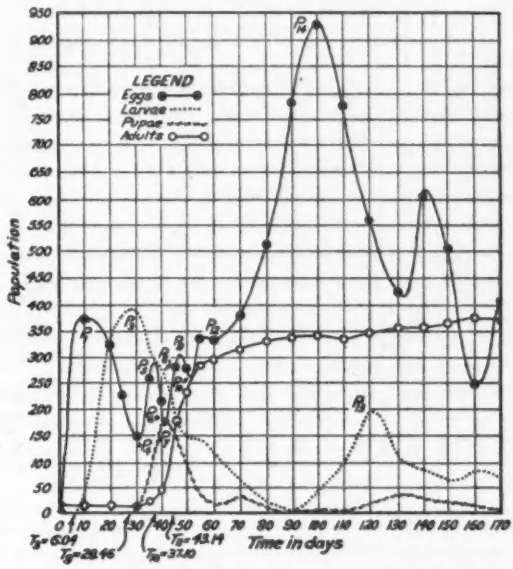


FIG. 7. *Smoothed curves for population growth of T. confusum, Duv. at 27°C.*

This periodic fluctuation in the numbers of eggs and larvae is believed to continue indefinitely. In the case of two populations grown at the University of Minnesota, owing to an infestation of intestinal parasites (*Gregarina*), pupae were unable to transform to immature adults, and slowly withered away a few days after pupation. In these two cases the egg and larval populations fluctuated regularly and repeatedly, with a period roughly equal to $\sum_{i=2}^{i=8} \Gamma_i$ while the adult population slowly dwindled away as explained on page 661. In such a case, the population as a whole would in time die out completely, unless the parasites decreased sufficiently to allow a few new adults to emerge. This special case will be described in a later paper.

Meanwhile, the adult population has risen to a maximum where $Z_{10}=0$ and from then on, slowly declines, while Z_{10} remains practically zero, as explained on page 661. It will be noticed that as N_{11} decreases, the amplitude of the pupal fluctuations becomes greater. While N_{11} remains greater than Y (see page 662) few or no pupae emerge, despite the brief increases in the pupal population, but as soon as N_{11} falls below Y, as explained above, a new production of adults begins the cycle again.

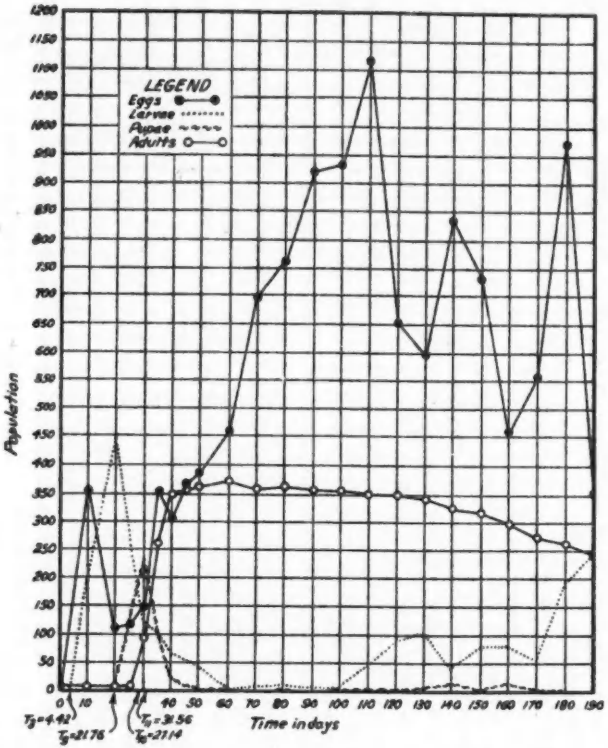


FIG. 8. *Population growth of T. confusum, Duv. at 32°C., mean of (A) and (B) populations.*

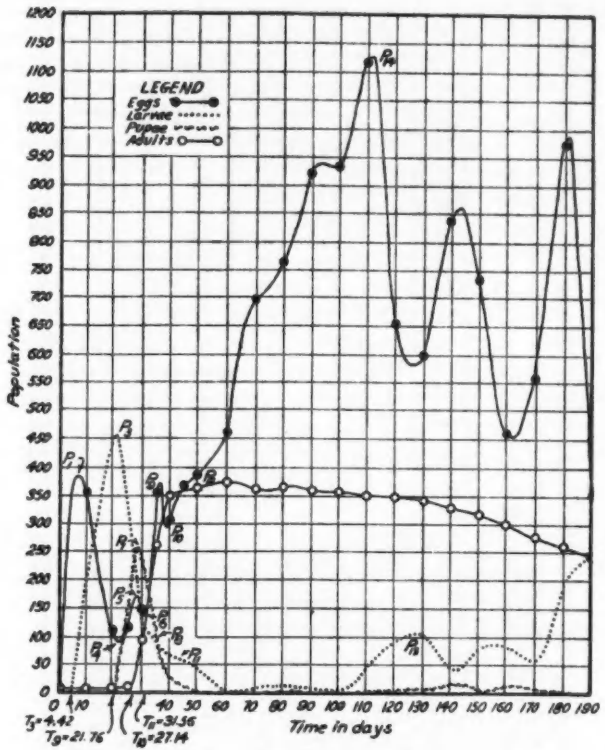


FIG. 9. *Smoothed curves for population growth of T. confusum, Duv. at 32°C.*

The writer does not believe that two identical cycles can ever follow one another in finite time, as the population at any instant is a function of its whole past history. It is highly probable however that succeeding cycles approach some fixed form, reaching the same after an infinite time.

Acknowledgment

The writer wishes to express his indebtedness to Dr. R. N. Chapman for the original suggestion of this problem, for the use of a great deal of biological data, and for his interest and encouragement in the working out of the problem, both at Minnesota and in Honolulu.

The writer is also indebted to Drs. R. W. Brink, Dunham Jackson, and W. Hart, of the Department of Mathematics, to Dr. Ross E. Gortner of the Dept. of Biochemistry and to Dr. MacDougall of the Department of Chemistry, all at the University of Minnesota; to Dr. E. U. Condon of the Department of Physics at the University of Princeton, to Dr. W. Carter of the Department of Entomology at the Experiment Station of the Association of Hawaiian Pineapple Canners at Honolulu, and to Dr. Paul Kirkpatrick of the Department of Physics at the University of Hawaii, for their assistance in matters connected with their own fields of work.

References

1. Allee, W. C. Animal Aggregations. Univ. of Chicago Press. 1931.
2. Bailey, V. A. The Interaction between hosts and parasites. Quart. J. of Math. Oxford Series 2: 1931.
3. Brindley, T. A. The growth and development of *Ephestia Kuehniella* Zeller (Lepidoptera) and *Tribolium confusum* Duv. (Coleoptera) under controlled conditions of temperature and relative humidity. Ann. Ent. Soc. Amer. 23: 741-757. 1930.
4. Chapman, R. N. The confused flour beetle. Annual Report No. 17. State Entomologist of Minn. 73-94. 1918.
5. Chapman, R. N. Insects infesting stored food products. Minn. Agric. Exp. Stn. Bull. 198: 45-50. 1921.
6. Chapman, R. N. Inhibiting the process of metamorphosis in the Confused Flour Beetle. Journ. Exp. Zool. 45: 293-299. 1926.
7. Chapman, R. N. Quantitative analysis of environmental factors. Ecology, 9: 111-122. 1928.
8. Gause, G. F. The influence of ecological factors on size of population. Amer. Nat. 45: 70-76. 1931.
9. Holdaway, F. G. Nutritional status and sex determination. Nature, 126: 131. 1930.
10. Loeb, L. B. Kinetic theory of gases. McGraw Hill, New York. 1927.
11. Park, T. Studies in population physiology. The relation of numbers to initial population growth in the flour beetle. *Tribolium confusum* Duv. Ecology, 13: 172-181. 1932.
12. Sweetman, M. D. and Palmer, L. S. Insects as test animals in vitamin research. I. Vitamin requirements of *Tribolium confusum* Duv. J. Biol. Chem. 77: 33-52. 1928.
13. Volterra, V. Variazioni e fluttuazioni del numero d'individui in specie animali conviventi. Accad. Naz. d. Lincei. Classe d. Sci. fisiche. mat. e nat. Ser. VI, vol. II fasc. III. 31-112. 1926.
14. Volterra, V. Variazioni e fluttuazioni del numero d'individui in specie animali conviventi. R. Com. Tal. Ital. N. 599. 1927.
15. Volterra, V. Leçons sur la théorie mathématique de la lutte pour la vie. Cahier. Sci. fasc. VII. 1931.